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(54) **STACKED PHOTOVOLTAIC DEVICE**

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(57) **ABSTRACT**

A stacked photovoltaic device comprises at least three p-i-n junction constituent devices superposed in layers, each having a p-type layer, an i-type layer and an n-type layer which are formed of silicon type non-single-crystal semiconductors. An amorphous silicon layer is used as the i-type layer of a first p-i-n junction, a microcrystalline silicon layer is used as the i-type layer of a second p-i-n junction and a microcrystalline silicon layer is used as the i-type layer of a third p-i-n junction, the first to third layers being in the order from the light-incident side.

A stacked photovoltaic device can be provided which is practicable and low-cost and yet has a high reliability, and also has a high photoelectric conversion efficiency.

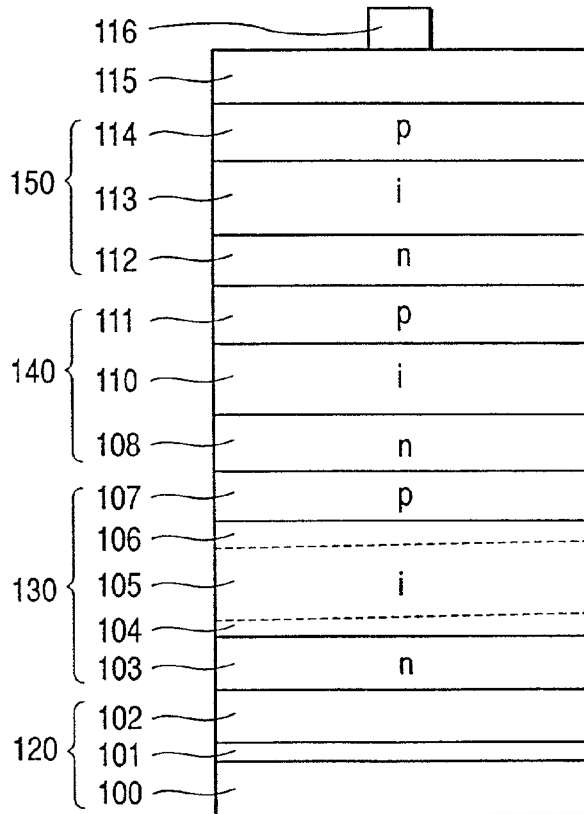


FIG. 1

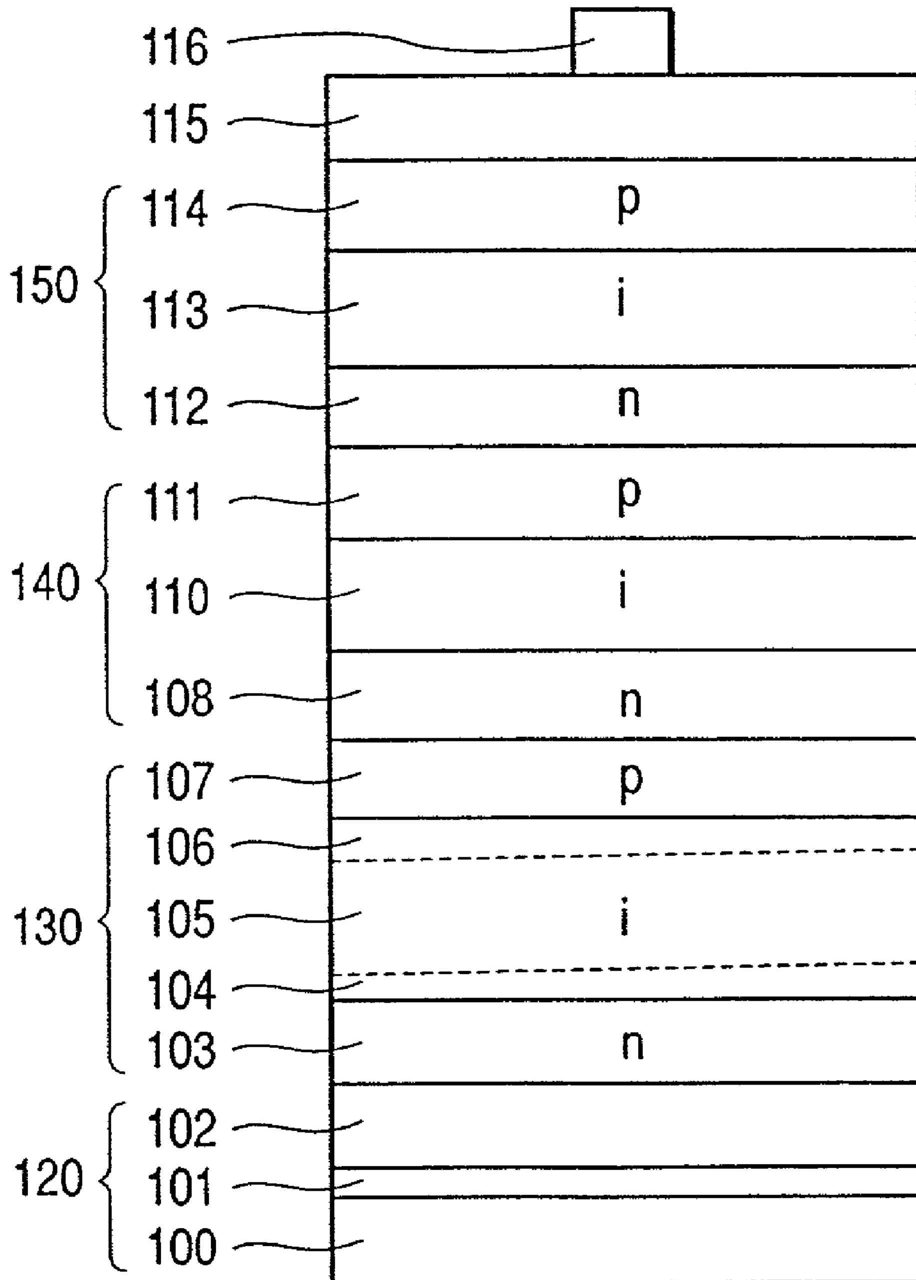


FIG. 2

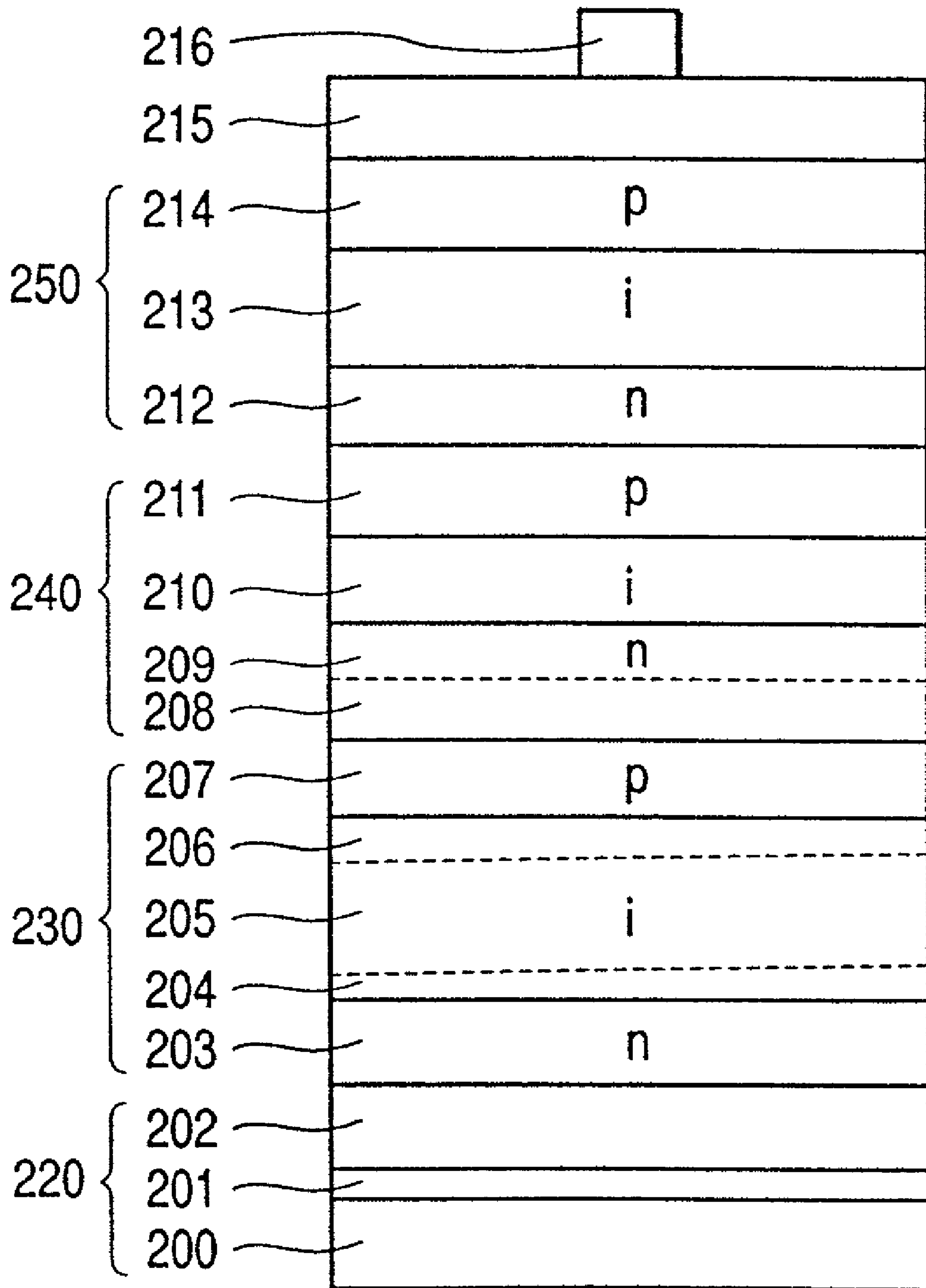
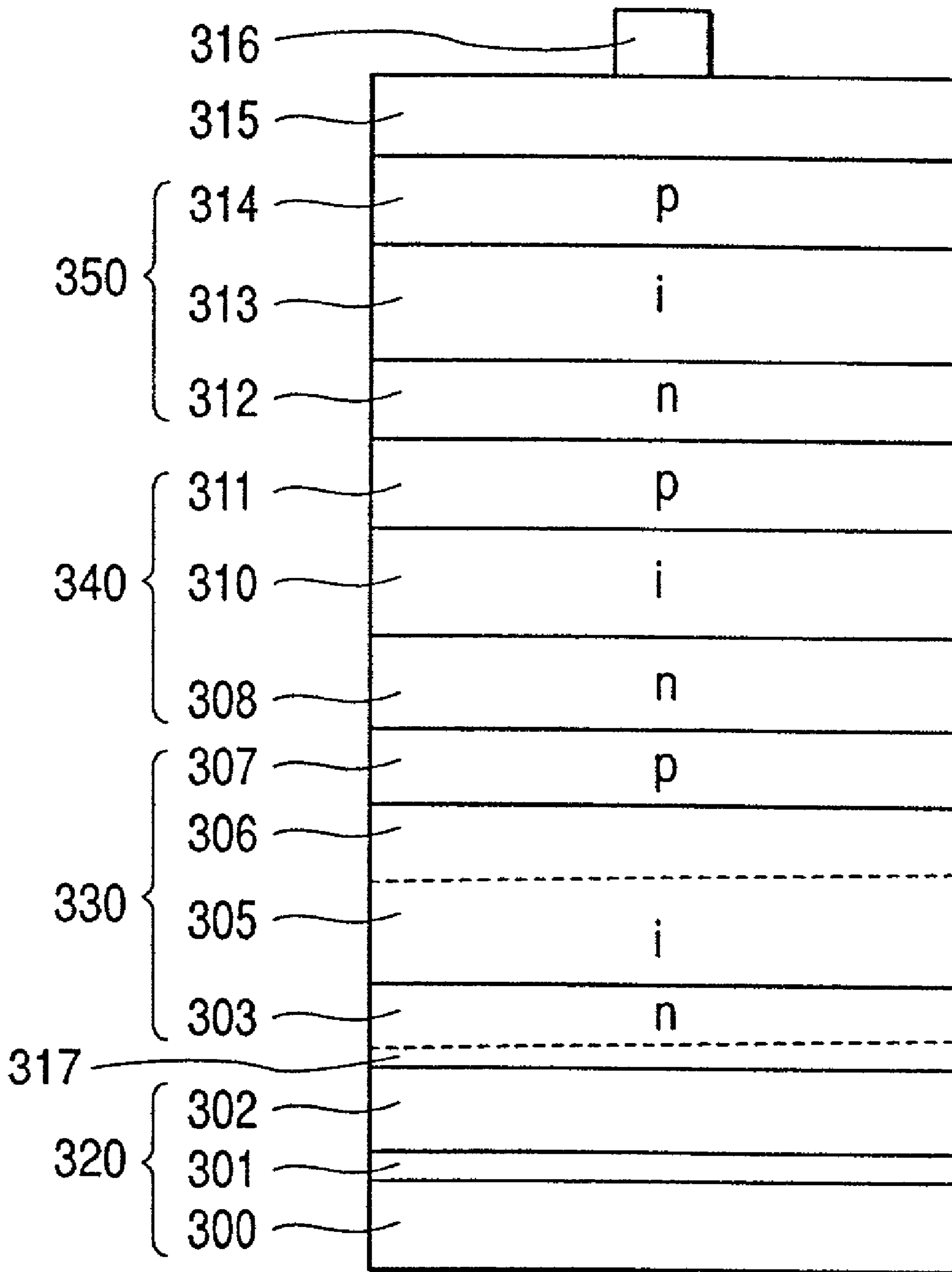


FIG. 3



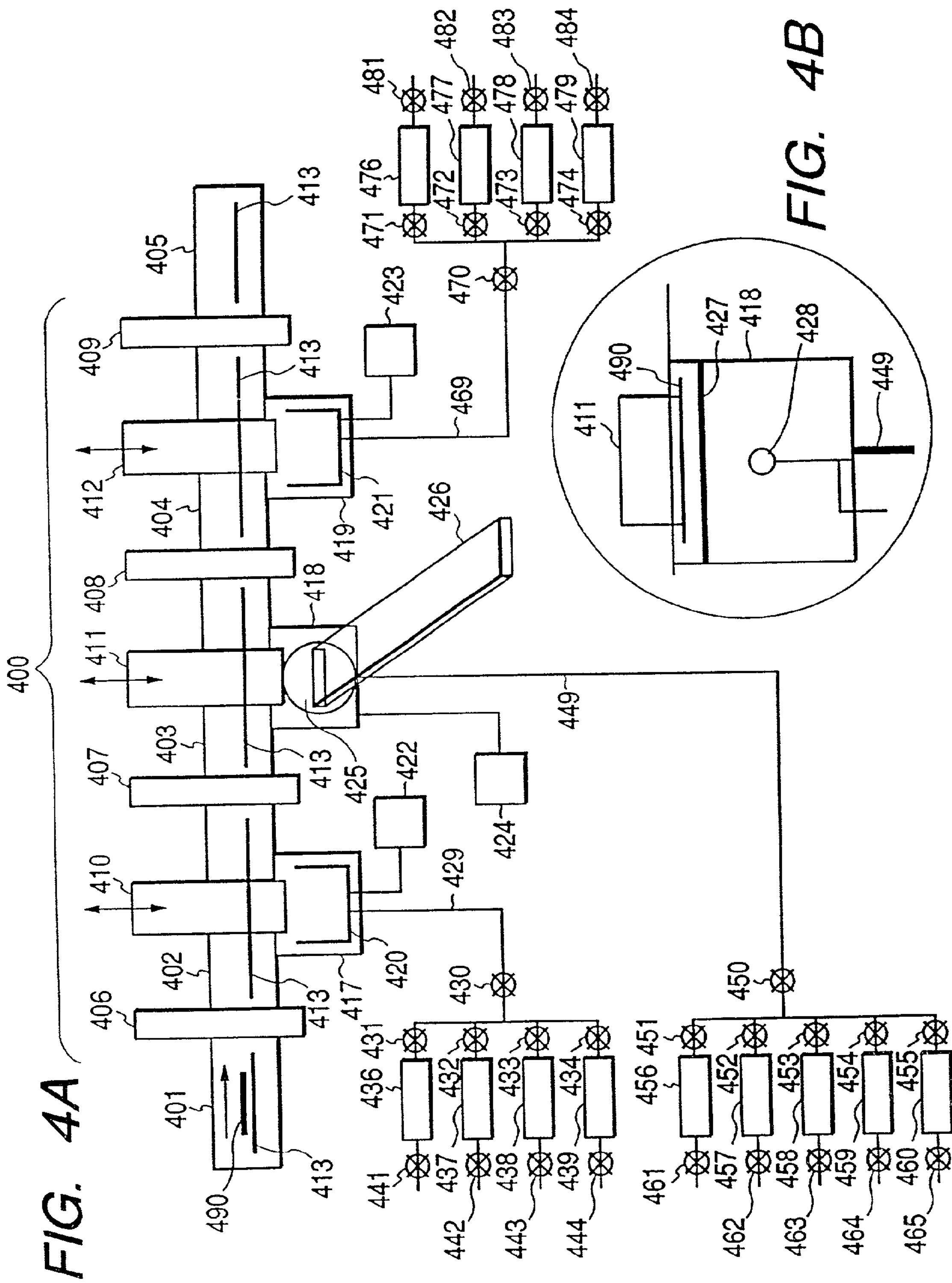


FIG. 4A

FIG. 4B

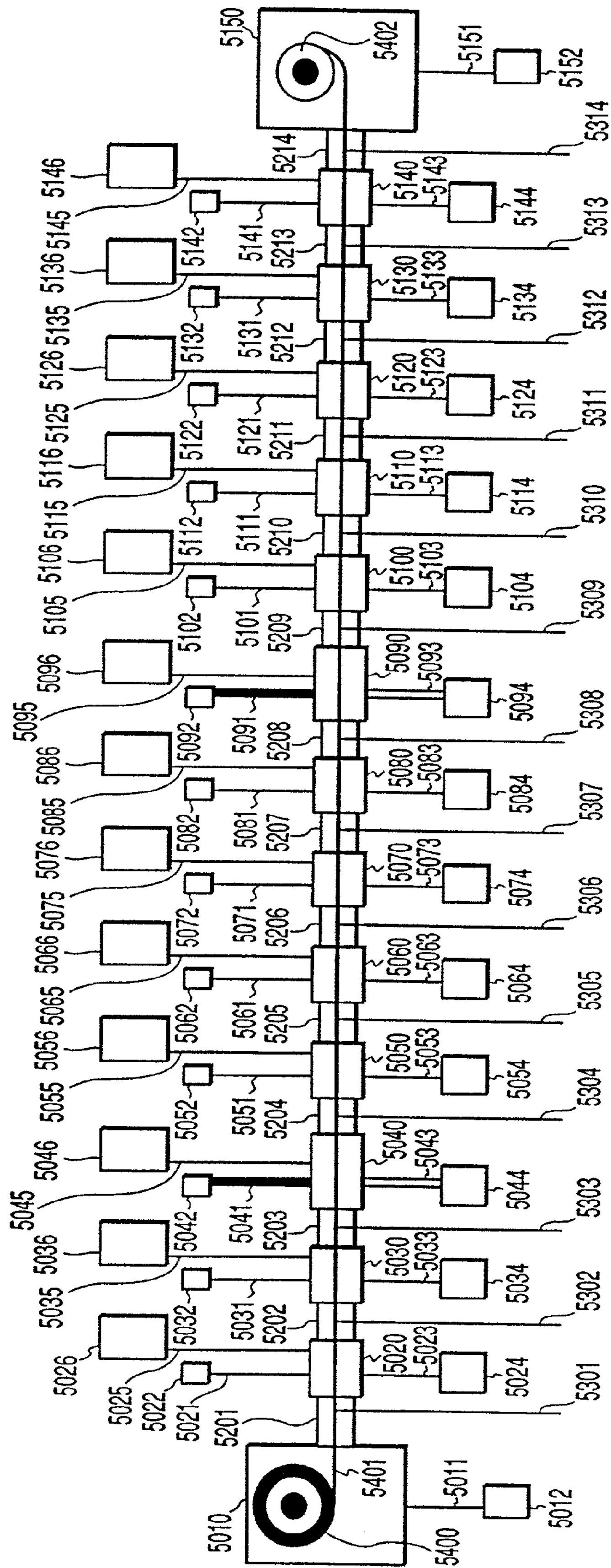


FIG. 5

STACKED PHOTOVOLTAIC DEVICE

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] This invention relates to a stacked photovoltaic device such as a solar cell and a photosensor, formed by superposing at least three p-i-n junction constituent devices each having a p-type layer, an i-type layer and an n-type layer which are formed of silicon type non-single-crystal semiconductors.

[0003] 2. Related Background Art

[0004] Photovoltaic devices which are photoelectric conversion devices that convert sunlight into electric energy are put into wide use as public-purpose power sources for low-power supply such as electronic calculators and wrist watches, and attract notice as practicable technique in future as substitute power for what is called petroleum fuel such as oil and coal.

[0005] Photovoltaic devices concern a technique that utilizes photovoltaic force attributable to p-n junction or the like of semiconductor devices. Semiconductors such as silicon absorb sunlight to produce photocarriers of electrons and holes. The photocarriers are caused to drift by the aid of an internal electric field at the p-n junction or the like and taken out to the outside.

[0006] Such photovoltaic devices are produced chiefly by using semiconductor fabrication processes. Stated specifically, a silicon single crystal whose valence electrons have been controlled to p-type or n-type is produced by a crystal growth process as exemplified by the CZ (Czokralski) process. The single crystal thus produced is sliced to prepare a silicon wafer of about 300 μm thick. A layer having different conductivity type is further superposed by, e.g., diffusing a valence electron control agent so as to have a conductivity type opposite to that of the wafer to provide p-n junction.

[0007] Now, at present, from the viewpoint of reliability and photoelectric conversion efficiency, single-crystal silicon is employed in principal photovoltaic devices having been put into practical use. However, since the production of such single-crystal silicon photovoltaic devices makes use of the semiconductor production process as stated above, it requires a high production cost.

[0008] The single-crystal silicon photovoltaic devices have additional disadvantages that the single-crystal silicon has a small optical absorption coefficient because of its indirect transition and hence must be formed in a thickness of at least 50 μm in order to absorb more sunlight, and that it has a band gap of about 1.1 eV, which is narrower than 1.5 eV suited for photovoltaic devices, and hence can not utilize short-wavelength components effectively.

[0009] Even if polycrystalline silicon is used to achieve a cost reduction, the problem of indirect transition still remains and the photovoltaic devices can not be made to have a smaller thickness. In addition, polycrystalline silicon also has problems ascribable to grain boundaries.

[0010] Moreover, since it is crystalline, wafers having large area can not be produced, making it difficult to make devices large-area. Hence, in order to withdraw a large electric power, unit devices must be connected by wiring in series or in parallel. Also, expensive packaging is necessary in order to protect photovoltaic devices from mechanical damage caused by various weather conditions when they are used outdoors. These make production cost higher per unit quantity of electricity generation than existing electricity generation systems. Such problems remain unsettled.

[0011] Under such circumstances, for the advancement of bringing photovoltaic devices into practical use as their use for electric power, it is an important technical subject to achieve cost reduction and make devices large-area. Various studies are made thereon, and researches are made on materials such as low-cost materials and materials with high photoelectric conversion efficiency.

[0012] Such materials for photovoltaic devices may include tetrahedral type amorphous semiconductors such as amorphous silicon, amorphous silicon germanium and amorphous silicon carbide, and compound semiconductors of Group II or VI such as CdS and Cu_2S and those of Group III or V such as GaAs and GaAlAs. In particular, thin-film photovoltaic devices in which amorphous semiconductors are used in photovoltaic layers have advantages that they can provide films having larger area than single-crystal photovoltaic devices, can be formed in a small layer thickness and can be deposited on any desired substrate materials, thus they are regarded as promising.

[0013] However, the photovoltaic devices making use of amorphous semiconductors still have problems in respect of improvement in photoelectric conversion efficiency and improvement in reliability.

[0014] As a means for improving the photoelectric conversion efficiency of the photovoltaic devices making use of amorphous semiconductors, for example, the band gap is made narrower so that the sensitivity to long-wavelength light can be made higher. More specifically, since amorphous silicon has a band gap of about 1.7 eV, it can not absorb light having wavelength of 700 nm or longer, and can not be utilized effectively. Accordingly, it is studied to employ narrow-band gap materials having a sensitivity to long-wavelength light.

[0015] Such materials may include amorphous silicon germanium, whose band gap can be changed arbitrarily from about 1.3 eV to about 1.7 eV with ease by changing the ratio of silicon material gas to germanium material gas at the time of film formation.

[0016] As another method for improving photoelectric conversion efficiency of photovoltaic devices, U.S. Pat. No. 2,949,498 discloses use of what is called a stacked cell in which photovoltaic devices having unit device structure are superposed in plurality. This stacked cell makes use of p-n junction crystal semiconductors. Its concept is common to both amorphous and crystalline, and to make sunlight spectra absorb more efficiently through photovoltaic devices having different band gaps and make Voc (open-circuit voltage) higher so that electricity generation efficiency can be improved.

[0017] In the stacked cell, constituent devices having different band gaps are superposed in plurality, and sunlight rays are absorbed efficiently at every part of their spectra so that photoelectric conversion efficiency can be improved. The cell is so designed that what is called the bottom layer,

positioned beneath what is called the top layer, has a narrower band gap than the band gap of the top layer, positioned on the light-incident side of the constituent devices superposed.

[0018] This has enabled sufficient absorption of sunlight spectra to bring about a dramatic improvement in photoelectric conversion efficiency (K. Miyachi et al., Proc. 11th E.C. Photovoltaic Solar Energy Conf., Montrieux, Switzerland, 88, 1992; and K. Nomoto et al., "a-Si Alloy Three Stacked Solar Cells with High Stabilized Efficiency", 7th Photovoltaic Science and Engineering Conf., Nagoya, 275, 1993).

[0019] Now, the above photovoltaic device is a device making use of amorphous semiconductors in all i-type layers, and hence it has had a limit to the prevention of what is called deterioration by light, a phenomenon in which photoelectric conversion efficiency becomes low because of irradiation by light. This is caused by amorphous silicon and amorphous silicon germanium whose film quality has lowered because of deterioration by light to come to have a poor carrier movability, and is a phenomenon peculiar to amorphous semiconductors which is not seen in crystal types. Accordingly, under existing circumstances, such a device has a poor reliability and hinders itself from being put into practical use, when used for electric power purpose.

[0020] In recent years, researches are also made not only on amorphous/amorphous types but also amorphous/crystalline types, and an improvement in photoelectric conversion efficiency is reported (Hamakawa, Y. et al., "Device Pysics and Optimum Design of a-Si/Poly-Si Tandem Solar Cells", Proceedings of 4th International PVSEC., pp.403-408, February 1989; (A. Shah, H. Keppner et al., "Intrinsic Microcrystalline Silicon (μc-Si:H)—A promising New Thin-film Solar Cell Material", IEEE First World Conference on Photovoltaic Energy Conversion, pp.409-412, December 1994; (Mitchel, R. L. et al., "The DOE/SERI Polycrystalline Thin-film Subcontract Program, "Processings of 20th IEEE Photovoltaic Specialists Conference, pp.1469-1476, September 1988).

[0021] However, taking account of the balance of electric currents of electricity generated by light in the stacked cell, the cell on the light-incident side (the side having a broad band gap) must be formed in a large layer thickness. This has not been well satisfactory from the viewpoint of deterioration by light.

[0022] Accordingly, it is sought to make amorphous photovoltaic devices much less undergo deterioration by light and to improve their photoelectric conversion efficiency after deterioration by light. In addition, in order to use them for electric power purpose, it is sought to more improve photoelectric conversion efficiency.

SUMMARY OF THE INVENTION

[0023] An object of the present invention is to provide a stacked photovoltaic device which is practicable and low-cost and yet has a high reliability, and also has a high photoelectric conversion efficiency.

[0024] To achieve the above object, the present invention provides a stacked photovoltaic device comprising at least three p-i-n junction constituent devices superposed in layers, each having a p-type layer, an i-type layer and an n-type layer which are formed of silicon type non-single crystal semiconductors, wherein;

> [0025] an amorphous silicon layer is used as the i-type layer of a first p-i-n junction, a microcrystalline silicon layer is used as the i-type layer of a second p-i-n junction and a microcrystalline silicon layer is used as the i-type layer of a third p-i-n junction; the first to third p-i-n junction layers being in the order from the light-incident side. (The "p-i-n junction" is herein meant to be a layer having p-i-n junction, i.e., a layer having regions of transition between p-type, i-type and n-type layers.)

[0026] The microcrystalline silicon layer which is the i-type layer of the second p-i-n junction may preferably have a layer thickness in the range of from 0.5 μm to 1.5 μm.

[0027] Meanwhile, the microcrystalline silicon layer which is the i-type layer of the third p-i-n junction may preferably have a layer thickness in the range of from 1.5 μm to 3.5 μm.

[0028] The microcrystalline silicon layer which is the i-type layer of the second p-i-n junction may preferably contain boron, and the boron may preferably be in a content not more than 8 ppm.

[0029] Meanwhile, the microcrystalline silicon layer which is the i-type layer of the third p-i-n junction may preferably contain boron, and the boron may preferably be in a content not more than 8 ppm.

[0030] The n-type layer of the second p-i-n junction may also preferably comprise a microcrystalline silicon layer, or a double layer consisting of a microcrystalline silicon layer and an amorphous silicon layer.

[0031] Meanwhile, the n-type layer of the third p-i-n junction may also preferably comprise a microcrystalline silicon layer, or a double layer consisting of a microcrystalline silicon layer and an amorphous silicon layer.

[0032] The microcrystalline silicon layers which are the i-type layers of the second and the third p-i-n junctions may preferably each have an optical absorption coefficient of 200 cm^{-1} or above at 950 nm.

[0033] The microcrystalline silicon layer which is the i-type layer of the second p-i-n junction may preferably be formed by plasma CVD (chemical vapor deposition) using a high frequency power of from 0.1 GHz to 10 GHz.

[0034] Meanwhile, the microcrystalline silicon layer which is the i-type layer of the third p-i-n junction may also preferably be formed by plasma CVD using a high frequency power of from 0.1 GHz to 10 GHz.

[0035] The stacked photovoltaic device of the present invention may preferably be formed by a roll-to-roll system in which the layers are superposed while transporting a continuous substrate stretched over a pair of rolls.

BRIEF DESCRIPTION OF THE DRAWINGS

[0036] **FIG. 1** is a schematic view for illustrating diagrammatically a cross sectional structure of an example of the stacked photovoltaic device according to the present invention.

[0037] **FIG. 2** is a schematic view for illustrating diagrammatically a cross sectional structure of another example of the stacked photovoltaic device according to the present invention.

[0038] **FIG. 3** is a schematic view for illustrating diagrammatically a cross sectional structure of still another example of the stacked photovoltaic device according to the present invention.

[0039] **FIG. 4** is a diagrammatic view for illustrating an example of a production system suited for forming the stacked photovoltaic device of the present invention continuously.

[0040] **FIG. 5** is a diagrammatic cross-sectional view for illustrating an example of a production system suited for forming the stacked photovoltaic device of the present invention continuously on a continuous substrate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0041] As stated previously, the present invention relates to a novel stacked photovoltaic device. The present invention will be described below in detail along its constitution and operation.

[0042] As a result of extensive studies on a stacked photovoltaic device that can solve the problems discussed above, may cause less deterioration by light and also has a high photoelectric conversion efficiency, the present inventors have reached the following findings.

[0043] In order to make the rate of deterioration by light lower and improve photoelectric conversion efficiency after deterioration by light while maintaining a high photoelectric conversion efficiency, among stacked photovoltaic devices, a stacked photovoltaic device is suited in which an amorphous silicon layer is used as the i-type layer of the first p-i-n junction, a microcrystalline silicon layer is used as the i-type layer of the second p-i-n junction and a microcrystalline silicon layer is used as the i-type layer of the third p-i-n junction; the first to third p-i-n junction layers being in the order from the light-incident side; i.e., an a-Si/μc-Si/μc-Si triple-type photovoltaic device.

[0044] The use of a microcrystalline silicon layer as the i-type layer of the second p-i-n junction and a microcrystalline silicon layer as the i-type layer of the third p-i-n junction brings about an improvement in semiconductor layers which have hitherto undergone a great deterioration by light in amorphous silicon type stacked photovoltaic devices and makes it possible to more restrain the deterioration by light than any conventional stacked photovoltaic devices.

[0045] The use of a microcrystalline silicon layer as the i-type layer of the third p-i-n junction also makes it possible to absorb long-wavelength light which has hitherto been relatively difficult to absorb, to achieve higher short-circuit current than any conventional stacked photovoltaic devices, and also to maintain a high photoelectric conversion efficiency.

[0046] With regard to the layer thickness of the microcrystalline silicon layer which is the i-type layer of the second p-i-n junction and/or the layer thickness of the microcrystalline silicon layer which is the i-type layer of the third p-i-n junction, making it/them smaller beyond the layer thickness having hitherto been considered suitable makes it possible to restrain localized levels in the i-type layer from increasing as a result of irradiation by light, to more restrain the deterioration by light than any conventional stacked photovoltaic devices and to improve photoelectric conversion efficiency after deterioration by light.

[0047] Incorporation of boron in the microcrystalline silicon layer which is the i-type layer of the second p-i-n junction and setting its content to be not more than 8 ppm, and/or incorporation of boron in the microcrystalline silicon layer which is the i-type layer of the third p-i-n junction and setting its content to be not more than 8 ppm make(s) it possible not to inhibit the growth of microcrystals and to improve the movability of holes at the time of electricity generation by light to thereby more restrain the deterioration by light than any conventional stacked photovoltaic devices and maintain a high photoelectric conversion efficiency.

[0048] Formation of the n-type layer of the second p-i-n junction by a microcrystalline silicon layer or by a double layer consisting of a microcrystalline silicon layer and an amorphous silicon layer and/or formation of the n-type layer of the third p-i-n junction by a microcrystalline silicon layer or by a double layer consisting of a microcrystalline silicon layer and an amorphous silicon layer make(s) it possible to form at a high deposition rate the microcrystalline silicon of the i-type layer formed on the n-type layer, to form good-quality microcrystalline silicon having less impurities and to maintain a high photoelectric conversion efficiency with less deterioration by light.

[0049] Making the microcrystalline silicon layers which are the i-type layers of the second and third p-i-n junctions each have an optical absorption coefficient of 200 cm^{-1} or above at 950 nm makes it possible to form the microcrystalline silicon layers which are the i-type layers of the second and third p-i-n junctions, in a layer thickness smaller beyond the layer thickness having hitherto been considered suitable, to restrain localized levels in the i-type layer from increasing as a result of irradiation by light, and to more restrain the deterioration by light than any conventional stacked photovoltaic devices. This also makes it possible to absorb long-wavelength light which has hitherto been relatively difficult to absorb, and to achieve higher photoelectric conversion efficiency than any conventional stacked photovoltaic devices.

[0050] With regard to the microcrystalline silicon layers which are the i-type layers of the second and third p-i-n junctions, their formation by plasma CVD using a high frequency power (microwaves or VHF waves) of from 0.1 GHz to 10 GHz, which enables discharging even at a high degree of vacuum, especially by controlling plasma condition at the deposition initial stage makes it possible to decompose and activate in a good efficiency material gases diluted with hydrogen in a large quantity, to restrain localized levels even at a high deposition rate to obtain good-quality microcrystalline silicon having a low defect density, and to more improve photoelectric conversion efficiency after deterioration by light of the triple-type photovoltaic device.

[0051] Formation of the stacked photovoltaic device of the present invention by a roll-to-roll system makes it possible to improve productivity very much.

[0052] The above stacked photovoltaic device of the present invention makes it possible to restrain deterioration by light, to make deterioration by light less occur while maintaining a high photoelectric conversion efficiency and to improve the photoelectric conversion efficiency after deterioration by light.

[0053] Preferred embodiments of the stacked photovoltaic device according to the present invention will be described below. The present invention is by no means limited to these embodiments.

[0054] In order to more improve photoelectric conversion efficiency of non-single-crystal silicon photovoltaic devices, to prevent deterioration by light and to improve reliability of non-single-crystal silicon photovoltaic devices, the present inventors have made the following studies.

[0055] First, as well known, in order to make deterioration by light less occur, it is effective to make up the photovoltaic device in a stacked form. However, it can not be said for the deterioration by light to have sufficiently been made to less occur. As a result of studies having been pushed on the constitution of the stacked photovoltaic device, the present inventors have reached the following findings.

[0056] One finding is that, among stacked photovoltaic devices, the deterioration by light can be more made to less occur in triple-type photovoltaic device in which three p-i-n junctions are superposed than in double-type photovoltaic devices in which two p-i-n junctions are superposed. This is presumably because, when semiconductor materials of the like types are used, the electric current of electricity generated by light is less produced for each p-i-n junction in the triple type than in the double type, so that the recombination of holes and electrons which are causative of the deterioration by light of amorphous semiconductors may less occur.

[0057] Another finding is that, among triple-type. photovoltaic devices, to reduce deterioration by light, the stacked photovoltaic device is most suited in which an amorphous silicon layer is used as the i-type layer of the first p-i-n junction, a microcrystalline silicon layer is used as the i-type layer of the second p-i-n junction and a microcrystalline silicon layer is used as the i-type layer of the third p-i-n junction; the first to third p-i-n junction layers being in the order from the light-incident side; i.e., the a-Si/μc-Si/μc-Si triple-type photovoltaic device. This is because the microcrystalline silicon layers each having an optical absorption coefficient of 200 cm^{-1} or above at 950 nm are used as the i-type layers of the second and third p-i-n junctions, which makes the deterioration by light much less occur than conventional non-single-crystal silicon triple-type photovoltaic devices.

[0058] Accordingly, the present inventors have pushed further studies on a-Si/μc-Si/μc-Si triple-type photovoltaic devices. As the result, it has proved to be preferable that, in order to make an a-Si/μc-Si/μc-Si triple-type photovoltaic device have the highest photoelectric conversion efficiency, the amorphous silicon layer which is the i-type layer of the first p-i-n junction may have a band gap of from 1.60 eV to 1.90 eV, the microcrystalline silicon layer which is the i-type layer of the second p-i-n junction may be formed in a layer thickness of from 0.5 μm to 1.5 μm and the microcrystalline silicon layer which is the i-type layer of the third p-i-n junction may be formed in a layer thickness of from 1.5 μm to 3.5 μm.

[0059] Here, it has been found that the amorphous silicon layer which is the i-type layer of the first p-i-n junction may have a layer thickness of from 500 to 2,500 angstroms, and more preferably from 700 to 1,500 angstroms. (Hereinafter, the first p-i-n junction is called "top cell", the second p-i-n junction "middle cell", and the third p-i-n junction "bottom cell").

[0060] The present inventors have pushed still further studies. Taking account of both the photoelectric conversion efficiency and the deterioration by light of the a-Si/μc-Si/μc-Si triple-type photovoltaic device, they have studied on how the rate of deterioration by light can be made lower while maintaining a high photoelectric conversion efficiency, i.e., how the photoelectric conversion efficiency after the lowering of photoelectric conversion efficiency due to deterioration by light has saturated (hereinafter simply "stabilized conversion efficiency") can be made maximum, in other words, on the best mode of the present invention.

[0061] Stacked photovoltaic devices are constituted of a plurality of p-i-n junctions connected in series. Hence, the values of electric current caused in the respective p-i-n junctions may be made as large as possible and also their respective values of electric current may be made close to one another, whereby a higher photoelectric conversion efficiency can be achieved.

[0062] For example, if the microcrystalline silicon layer which is the i-type layer of the middle cell of the a-Si/μc-Si/μc-Si triple-type photovoltaic device is formed in a layer thickness smaller than 0.5 μm, the electric current may be less caused by light to tend to cause a decrease in photoelectric conversion efficiency as a triple cell. If on the other hand it is formed in a layer thickness larger than 1.5 μm, the middle cell can cause electric current sufficiently but the light may enter the bottom cell in a small quantity, resulting in a small quantity of electric current caused in the bottom cell to tend to cause a decrease in photoelectric conversion efficiency as a triple cell.

[0063] If the microcrystalline silicon layer which is the i-type layer of the bottom cell is formed in a layer thickness smaller than 1.5 μm, the electric current may be less caused by light to tend to cause a decrease in photoelectric conversion efficiency as a triple cell. If on the other hand it is formed in a layer thickness larger than 3.5 μm, it may affect the carrier movability adversely at the time of electricity generation by light, resulting in a lowering of FF (fill factor) of the bottom cell to tend to cause a decrease in photoelectric conversion efficiency as a triple cell.

[0064] Repetition of such studies has revealed that the microcrystalline silicon layer as the i-type layer of the middle cell may preferably be formed in a thickness of from 0.5 μm to 1.5 μm, and more preferably from 0.6 μm to 1.2 μm.

[0065] It has also revealed that the microcrystalline silicon layer as the i-type layer of the bottom cell may preferably be formed in a thickness of from 1.5 μm to 3.5 μm, and more preferably from 1.7 μm to 3.3 μm.

[0066] Incorporation of boron in an amount not more than 8 ppm in the microcrystalline silicon layer which is the i-type layer of the middle cell also makes it possible to improve the movability of holes at the time of electricity generation by light without inhibiting the growth of micro-

crystals of the microcrystalline silicon and while controlling any lowering of film quality which may be caused by excessive inert boron. This has made it possible to maintain a high photoelectric conversion efficiency while controlling the deterioration by light.

[0067] In addition, similarly, the incorporation of boron in an amount not more than 8 ppm in the microcrystalline silicon layer which is the i-type layer of the bottom cell makes it possible to improve the movability of holes at the time of electricity generation by light without inhibiting the growth of microcrystals of the microcrystalline silicon and while controlling any lowering of film quality which may be caused by excessive inert boron. This has made it possible to maintain a high photoelectric conversion efficiency while controlling the deterioration by light.

[0068] Formation of the n-type layer of the middle cell by a microcrystalline silicon layer or by a double layer consisting of a microcrystalline silicon layer and an amorphous silicon layer makes it possible to form at a high deposition rate the microcrystalline silicon of the i-type layer formed on the n-type layer, to form good-quality microcrystalline silicon while restraining impurities from mixing as far as possible. Also, the microcrystalline silicon of the i-type layer formed on the n-type layer is formed as a good-quality microcrystalline silicon having less amorphous silicon component from the beginning of deposition, and also the n-type semiconductor layer is formed by a microcrystalline silicon layer or by a double layer consisting of a microcrystalline silicon layer and an amorphous silicon layer. This makes it possible to deposit the microcrystalline silicon of the i-type layer at a temperature relatively higher than the deposition substrate temperature that has hitherto been studied, so that microcrystalline silicon with a better film quality can be formed. In addition, the formation of the n-type layer by a microcrystalline silicon layer or by a double layer consisting of a microcrystalline silicon layer and an amorphous silicon layer makes it possible to less cause the damage to n-type layer which may be caused by hydrogen ions included at the initial stage of deposition of microcrystalline silicon of the i-type layer. This has made it possible to make the deterioration by light less occur and to maintain a high photoelectric conversion.

[0069] Formation of the n-type layer of the bottom cell by a microcrystalline silicon layer or by a double layer consisting of a microcrystalline silicon layer and an amorphous silicon layer also makes it possible to form at a high deposition rate the microcrystalline silicon of the i-type layer formed on the n-type layer, to form good-quality microcrystalline silicon while restraining impurities from mixing as far as possible. Also, the microcrystalline silicon of the i-type layer formed on the n-type layer is formed as a good-quality microcrystalline silicon having less amorphous silicon component from the beginning of deposition, and also the n-type layer is formed by a microcrystalline silicon layer or by a double layer consisting of a microcrystalline silicon layer and an amorphous silicon layer. This makes it possible to deposit the microcrystalline silicon of the i-type layer at a temperature relatively higher than the deposition substrate temperature that has hitherto been studied, so that microcrystalline silicon with a better film quality can be formed. In addition, the formation of the n-type layer by a microcrystalline silicon layer or by a double layer consisting of a microcrystalline silicon layer and an amorphous silicon layer makes it possible to less cause the damage to n-type layer which may be caused by hydrogen ions included at the initial stage of deposition of microcrystalline silicon of the i-type layer. This has made it possible to make the deterioration by light less occur and to maintain a high photoelectric conversion.

[0070] It has also been found that, even when the microcrystalline silicon layer which is the i-type layer of the bottom cell is formed in the layer thickness made smaller up to the above value, the value of electric current caused in the bottom cell can be maintained by making the microcrystalline silicon have a large optical absorption coefficient.

[0071] It has still also been found that, even when the microcrystalline silicon layer which is the i-type layer of the bottom cell is formed in the layer thickness made smaller up to the above value, the value of electric current caused in the bottom cell can be maintained by making the microcrystalline silicon have an optical absorption coefficient of 200 cm^{-1} or above at 950 nm.

[0072] Stated specifically, it has been found that the value of electric current caused in the bottom cell can be maintained by forming the bottom cell i-type layer microcrystalline silicon layer at a higher deposition substrate temperature or by changing the rate of dilution with hydrogen.

[0073] Use of the microcrystalline silicon in the i-type layers of the middle and bottom cells has made it possible to make open-circuit voltage (Voc) relatively high, which has hitherto been questioned as being low, and to maintain a high photoelectric conversion efficiency.

[0074] An amorphous silicon layer or amorphous silicon carbide layer provided between the p-type layer and the microcrystalline silicon layer in each of the middle cell and bottom cell has the function chiefly to improve open-circuit voltage (Voc) of -the photovoltaic device. This is presumably because the amorphous silicon layer or amorphous silicon carbide layer makes large the diffusion potential of the p-i-n junction. It can also be presumed that such layer forms a barrier which prevents the electrons produced by light in the microcrystalline silicon, from diffusing into the p-type layer.

[0075] The amorphous silicon layer or amorphous silicon carbide layer may preferably be formed in a layer thickness of from 30 angstroms to 450 angstroms, and more preferably from 50 angstroms to 350 angstroms. The amorphous silicon layer or amorphous silicon carbide layer provided in such a measure of layer thickness has little caused an increase in the rate of deterioration by light of the photovoltaic device.

[0076] As a result of further extensive studies made by the present inventors, the formation of microcrystalline silicon by plasma CVD using a high frequency power of from 0.1 GHz to 10 GHz and also by optimizing formation conditions has made it possible to obtain good-quality microcrystalline silicon having a small defect density. As the result, it has become possible to improve photoelectric conversion efficiency of the photovoltaic device in which the microcrystalline silicon is used in the i-type layer and also to make its deterioration by light less occur, i.e., to improve the stabilized conversion efficiency.

[0077] This has been achieved by the formation of microcrystalline silicon by plasma CVD using a high frequency

power of from 0.1 GHz to 10 GHz (VHF plasma CVD or microwave plasma CVD) and also by optimizing formation conditions, whereas the microcrystalline silicon is formed by RF plasma CVD in almost all conventional devices. It is considered that the use of such a high frequency power makes material gas decomposition efficiency high, makes decomposition efficiency high especially when material gases are fed in a large quantity in order to enhance deposition rate, and makes hydrogen become decomposed at a high rate under large-quantity dilution with hydrogen so as to be activated with ease, so that the mobility of precursors at the growth surface of thin film being deposited has become greater to have enabled the formation of good-quality microcrystalline silicon.

[**0078**] It is also considered that, when the microcrystalline silicon is formed by the plasma CVD using a high frequency power of from 0.1 GHz to 10 GHz, films can be formed at a higher rate and therefore at a higher substrate temperature than when RF plasma CVD is used, to have enabled the formation of good-quality microcrystalline silicon.

[**0079**] Use of relatively high-temperature-deposited good-quality microcrystalline silicon in the i-type layer of the bottom cell, formed by the plasma CVD using a high frequency power of from 0.1 GHz to 10 GHz has made it possible to restrain any thermal damage to the minimum in the course the middle cell is formed, and to less cause the deterioration by light while maintaining a high photoelectric conversion efficiency as a triple cell, i.e., to improve the stabilized conversion efficiency.

[**0080**] Combination of what is called the roll-to-roll system with the above plasma CVD using a high frequency power of from 0.1 GHz to 10 GHz, the former being a system in which thin films are formed on the surface of a substrate while transporting a belt-like substrate continuously, also has made it possible to reduce the localized levels in the vicinity of interfaces between a plurality of semiconductor layers to improve photoelectric conversion efficiency of the photovoltaic device.

[**0081**] **FIG. 1** illustrates diagrammatically a cross sectional structure of an example of the stacked photovoltaic device according to the present invention. The stacked photovoltaic device shown in **FIG. 1** has a structure wherein three p-i-n junctions are superposed on a substrate **120**. Reference numeral **150** denotes a first p-i-n junction (top cell); **140**, a second p-i-n junction (middle cell); and **130**, a third p-i-n junction (bottom cell); which are in the order from the light-incident side.

[**0082**] These three p-i-n junctions are superposed on a substrate **120** comprising a base member **100** and formed thereon a metal layer **101** and a transparent conductive layer **102**, and a transparent electrode **115** and a collector electrode **116** are formed at the uppermost part of the three p-i-n junctions to form the stacked photovoltaic device.

[**0083**] These p-i-n junctions are comprised respectively of an n-type layer **112**, n-type microcrystalline semiconductor layers **103** and **108**, an i-type layer **113**, i-type microcrystalline semiconductor layers **105** and **110**, i-type buffer layers **104** and **106**, and p-type layers **107**, **111** and **114**.

[**0084**] In this photovoltaic device, amorphous silicon is used as the i-type layer **113** of the first p-i-n junction, microcrystalline silicon is used as the i-type layer **110** of the second p-i-n junction and microcrystalline silicon is used as the i-type layer **105** of the third p-i-n junction.

[**0085**] **FIG. 2** illustrates diagrammatically a cross sectional structure of another example of the stacked photovoltaic device according to the present invention. The stacked photovoltaic device shown in **FIG. 2** has a structure wherein three p-i-n junctions are superposed on a substrate **220**. Reference numeral **250** denotes a first p-i-n junction (top cell); **240**, a second p-i-n junction (middle cell); and **230**, a third p-i-n junction (bottom cell); which are in the order from the light-incident side.

[**0086**] These three p-i-n junctions are superposed on a substrate **220** comprising a base member **200** and formed thereon a metal layer **201** and a transparent conductive layer **202**, and transparent electrode **215** and a collector electrode **216** are formed at the uppermost part of the three p-i-n junctions to form the stacked photovoltaic device.

[**0087**] These p-i-n junctions are comprised respectively of n-type layers **208** and **212**, n-type microcrystalline semiconductor layers **203** and **209**, an i-type layer **213**, i-type microcrystalline semiconductor layers **205** and **210**, i-type buffer layers **204** and **206**, and p-type layers **207**, **211** and **214**.

[**0088**] In this photovoltaic device, too, amorphous silicon is used as the i-type layer **213** of the first p-i-n junction, microcrystalline silicon is used as the i-type layer **210** of the second p-i-n junction and microcrystalline silicon is used as the i-type layer **205** of the third p-i-n junction.

[**0089**] **FIG. 3** illustrates diagrammatically a cross sectional structure of still another example of the stacked photovoltaic device according to the present invention. The stacked photovoltaic device shown in **FIG. 3** has a structure wherein three p-i-n junctions are superposed on a substrate **320**. Reference numeral **350** denotes a first p-i-n junction (top cell); **340**, a second p-i-n junction (middle cell); and **330**, a third p-i-n junction (bottom cell); which are in the order from the light-incident side.

[**0090**] These three p-i-n junctions are superposed on a substrate **320** comprising a base member **300** and formed thereon a metal layer **301** and a transparent conductive layer **302**, and a transparent electrode **315** and a collector electrode **316** are formed at the uppermost part of the three p-i-n junctions to form the stacked photovoltaic device.

[**0091**] These p-i-n junctions are comprised respectively of n-type layers **317** and **312**, n-type microcrystalline semiconductor layers **303** and **308**, an i-type layer **313**, i-type microcrystalline semiconductor layers **305** and **310**, an i-type buffer layer **306**, and p-type layers **307**, **311** and **314**.

[**0092**] In this photovoltaic device, too, amorphous silicon is used as the i-type layer **313** of the first p-i-n junction, microcrystalline silicon is used as the i-type layer **310** of the second p-i-n junction and microcrystalline silicon is used as the i-type layer **305** of the third p-i-n junction.

[**0093**] The stacked photovoltaic devices shown in FIGS. **1** to **3** may also have layer configurations wherein the n-type semiconductor layers (inclusive of n-type microcrystalline semiconductor layers) and p-type semiconductor layers in the p-i-n junctions are replaced with one another.

[**0094**] The constituents of the stacked photovoltaic device of the present invention will be further detailed below with reference to **FIG. 1**.

[0095] (Substrate)

[0096] Since the semiconductor layers **103** to **114** are thin films of about 3 μm at most in total thickness, they are deposited on a suitable substrate. The base member **100** used in such a substrate may be either single-crystal or non-single-crystal, and also may be either electrically conductive or electrically insulating. The base member **100** may further be either light-transmitting or non-light-transmitting, but may preferably be free from deformation or strain and have a desired strength.

[0097] It may specifically include thin sheets of metals such as Fe, Ni, Cr, Al, Mo, Au, Nb, Ta, V, Ti, Pt and Pb and alloys thereof as exemplified by bronze and stainless steel, and composites of these; films or sheets of heat-resistant synthetic resins such as polyester, polyethylene, polycarbonate, cellulose acetate, polypropylene, polyvinyl chloride, polyvinylidene chloride, polystyrene, polyamide, polyimide and epoxy, or composites of any of these with glass fiber, carbon fiber, boron fiber or metal fiber; any of these materials subjected to surface coating by sputtering, vapor deposition or plating to cover their surfaces with a metal thin film formed of a different kind of material and/or an insulating thin film formed of SiO_2, Si_3N_4, Al_2O_3, AlN; and glasses and ceramics.

[0098] In use as a substrate for the photovoltaic device, when the base member **100** is made of an electrically conductive material such as a metal, it may serve as an electrode for collecting electric currents directly. When it is made of an electrically insulating material such as a synthetic resin, its surface on the side where deposited films are formed may preferably previously be surface-treated by plating, vapor deposition or sputtering of a single metal, an alloy or a transparent conductive oxide (TCO), such as Al, Ag, Pt, Au, Ni, Ti, Mo, W, Fe, V, Cr, Cu, stainless steel, bronze, nichrome, SnO_2, In_2O_3, ZnO and ITO (indium-tin oxide) to form an electrode for collecting electric currents. Such an electrode may be formed as the metal layer **101** and/or the transparent conductive layer **102**.

[0099] Of course, also when the base member **100** is made of the electrically conductive material such as a metal, a different kind of metal layer may be provided on the base member **100** on its side where the deposited films are formed, in order to, e.g., improve reflectance of long-wavelength light on the surface of the substrate and prevent constituent elements from their mutual diffusion between the substrate material and the deposited films. When the base member **100** is relatively transparent and the photovoltaic device has a layer configuration wherein the light is made incident on the side of the base member **100**, a light-transmissive conductive thin film such as the above transparent conductive oxide or metal thin film may preferably previously be formed by deposition.

[0100] With regard to the surface properties of the base member **100**, it may have a smooth surface, or may have a finely uneven surface. When the substrate has a finely uneven surface, it may have spherical, conical or pyramidical unevenness with its maximum height (Rmax) of preferably from 0.05 μm to 2 μm. This makes the reflection of light from the surface irregular to bring about an increase in optical path length of the reflected light. The base member may have the shape of, e.g., a plate, continuous-sheet belt or cylinder having a smooth surface or uneven surface depending on purposes. Its thickness may be so determined appropriately that the photovoltaic device as desired can be formed. It may have a thickness as small as possible so long as the function as the base member can be exhibited well, when the photovoltaic device is required to have a flexibility or when light is made incident on the side of the base member. However, taking account of the production and handling of the base member and in view of its mechanical strength, it may usually have a thickness of at least 10 μm.

[0101] (Metal Layer, Transparent Conductive Layer)

[0102] The metal layer **101** used in the present invention is commonly an electrode (back surface electrode) provided on the back surface of the semiconductor layers against the light-incident direction. Hence, it is provided at the position of **101** in **FIG. 1** or, in the case where the base member **100** is light-transmissive and the light is made incident on the side of the substrate, it is provided at the position of **115**.

[0103] Materials for the metal layer **101** include metals such as gold, silver, copper, aluminum, nickel, iron, chromium, molybdenum, tungsten, titanium, cobalt, tantalum, niobium and zirconium, or alloys such as stainless steel. In particular, metals having a high reflectance, such as aluminum, copper, silver and gold are particularly preferred. When the metals having a high reflectance are used, the back surface electrode may be made to serve also as a light-reflecting layer that reflects the light having not been absorbed completely in the semiconductor layers, to return it to the semiconductor layers.

[0104] The metal layer **101** may have a flat shape, and may more preferably have an uneven shape to cause the light to scatter. In the case of the metal layer having such light-scattering uneven shape, any long-wavelength light having not been absorbed completely in the semiconductor layers can be scattered to elongate optical paths in the semiconductor layers, so that the photovoltaic device can be improved in its sensitivity to long-wavelength light to increase short-circuit currents and can be improved in photoelectric conversion efficiency. As to the light-scattering uneven shape, the difference in height (Rmax) between hills and valleys of the unevenness may preferably be from 0.2 μm to 2.0 μm.

[0105] When, however, the base member **100** serves also as the back surface electrode, it is unnecessary in some cases to form the metal layer **101**.

[0106] The metal layer **101** may be formed by vapor deposition, sputtering, plating or printing. When the metal layer **101** is formed to have the light-scattering uneven shape, the metal or alloy film thus formed may be dry-etched or wet-etched, or sand-blasted or heated, to form the unevenness. Alternatively, the above metal or alloy may be vapor-deposited on the base member **100** while heating it to provide the light-scattering uneven shape.

[0107] A transparent conductive layer **102** formed of conductive zinc oxide or the like may also be provided between the metal layer **101** and the n-type microcrystalline semiconductor layer **103**. The transparent conductive layer **102** has the effect of not only preventing the metal elements constituting the metal layer **101** from their diffusion into the n-type microcrystalline semiconductor layer, but also, when endowed with a little resistance, preventing short circuit from being caused by defects such as pinholes between the

metal layer **101** and the transparent electrode **115** which are provided so as to hold the semiconductor layers between them, and also confining in the photovoltaic device the light made incident after multiple interference is caused by thin films.

[**0108**] (i-Type layer: Intrinsic Semiconductor Layer)

[**0109**] In photovoltaic devices making use of IV-IV group and III-V group alloy type amorphous semiconductor materials, the i-type layer used in the p-i-n junction is an important layer that responses to irradiation light to cause and transport carriers.

[**0110**] A slightly p-type or slightly n-type layer may also be used as the i-type layer.

[**0111**] IV-IV group and III-V group alloy type amorphous semiconductor materials contain hydrogen atoms (H,D) or halogen atoms (X) and these have important action. The hydrogen atoms (H,D) or halogen atoms (X) contained in the i-type layer act to compensate unbonded arms (dangling bonds) in the i-type layer to improve the product of mobility and lifetime of carriers in the i-type layer. They also act to compensate interfacial energy levels of the interfaces between p-type layer and i-type layer and between n-type layer and i-type layer, and improves the photovoltaic effect of photovoltaic, photoelectric currents and photo-responsitivity of the photovoltaic device.

[**0112**] The hydrogen atoms and/or halogen atoms contained in the i-type layer may be in an amount of from 1 to 40 atom % as an optimum content. In particular, as a preferable form of distribution, the hydrogen atoms and/or halogen atoms may be distributed in a larger content on the side of the interfaces between p-type layer and i-type layer and between n-type layer and i-type layer, In the vicinity of the interfaces, the hydrogen atoms and/or halogen atoms may be contained in an amount 1.05 to 2 times their content in the bulk, as a preferable range. It is also preferable that the content of the hydrogen atoms and/or halogen atoms changes correspondingly to the content of silicon atoms.

[**0113**] In the photovoltaic device of the present inventions amorphous silicon is used as the semiconductor material constituting the i-type layer **113** of the first p-i-n junction **150**. Microcrystalline silicon is used as the semiconductor material constituting the i-type layer **110** of the second p-i-n junction **140**. Microcrystalline silicon is used as the semiconductor material constituting the i-type layer **105** of the third p-i-n junction **130**.

[**0114**] The amorphous silicon and microcrystalline silicon are represented as a-Si:H, a-Si:F, a-Si:H:F, μc-Si:H, μc-Si:F or μc-Si:H:F in accordance with the element(s) that compensates dangling bonds.

[**0115**] Stated more specifically, as a material for the i-type layer **113** of the first p-i-n junction **150** preferred in the stacked photovoltaic device of the present invention, it may include i-type amorphous silicon hydride (a-Si:H), having characteristics such as an optical band gap (Eg) of from 1.60 eV to 1.90 eV, a hydrogen atom content (C_H) of from 1.0% to 25.0%, a photoconductivity (σp) of 1.0×10^{-5} S/cm or above under irradiation by solor simulator of AM 1.5 and 100 mW/cm^2, a dark conductivity (ad) of 1.0×10^{-9} S/cm or below, an Urbach energy of 55 meV or below as measured by the constant photocurrent method (CPM), and a localized level density of 10^{17}/cm^3 or below. Such a material may preferably be used.

[**0116**] The microcrystalline silicon constituting the i-type layer **110** of the second p-i-n junction **140** of the photovoltaic device according to the present invention may preferably be in a layer thickness of from 0.5 μm to 1.5 μm. The microcrystalline silicon constituting the i-type layer of the second p-i-n junction may preferably contain boron in an amount not more than 8 ppm. Also, the microcrystalline silicon layer which is the i-type layer of the second p-i-n junction may preferably have an optical absorption coefficient of 200 cm^{-1} or above at 950 nm. The microcrystalline silicon layer which is the i-type layer of the second p-i-n junction may also preferably be a layer formed by plasma CVD making use of a high frequency power of from 0.1 GHz to 10 GHz.

[**0117**] The microcrystalline silicon constituting the i-type layer **105** of the third p-i-n junction **130** of the photovoltaic device according to the present invention may preferably be in a layer thickness of from 1.5 μm to 3.5 μm. The microcrystalline silicon constituting the i-type layer of the third p-i-n junction may preferably contain boron in an amount not more than 8 ppm. Also, the microcrystalline silicon layer which is the i-type layer of the third p-i-n junction may preferably have an optical absorption coefficient of 200 cm^{-1} or above at 950 nm. The microcrystalline silicon layer which is the i-type layer of the third p-i-n junction may also preferably be a layer formed by plasma CVD making use of a high frequency power of from 0.1 GHz to 10 GHz.

[**0118**] (p-Type Layer or n-Type Layer)

[**0119**] The p-type layer or n-type layer also is an important layer that influences the characteristics of the stacked photovoltaic device of the present invention.

[**0120**] Amorphous materials (herein simply "a-") and microcrystalline materials (herein simply "μc-") of the p-type layer or n-type layer may include, e.g., materials such as a-Si:H, a-Si:HX, a-SiC:H, a-SiC:HX, a-SiGe:H, a-SiGeC:H, a-SiO:H, a-SiN:H, a-SiON:HX, a-SiOCN:HX, μc-Si:H, μc-SiC:H, μc-SiHX, μc-SiC:HX, μc-SiGe:H, μc-SiO:H, μc-SiGeC:H, μc-SiN:H, μc-SiON:HX and μc-SiOCN:HX (X is a halogen atom) to which a p-type valence electron control agent (Group III atom of the periodic table, B, Al, Ga, In or Tl) or an n-type valence electron control agent (Group V atom of the periodic table, P, As, Sb or Bi) has been added in a high concentration. These materials may also be used as materials for the i-type layer described above, without addition of the valence electron control agent.

[**0121**] The polycrystalline materials (herein simply "poly-") may include materials such as poly-Si:H, poly-Si:HX, poly-SiC:H, poly-SiC:HX, poly-SiGe:H, poly-Si, poly-SiC and poly-SiGe to which a p-type valence electron control agent (Group III atom of the periodic table, B, Al, Ga, In or Ti) or an n-type valence electron control agent (Group V atom of the periodic table, P, As, Sb or Bi) has been added in a high concentration.

[**0122**] A crystalline semiconductor layer having less absorbance or an amorphous semiconductor layer having a broad band gap is suited especially for the p-type layer or n-type layer on the light-incident side.

[0123] The addition of the Group III atom of the periodic table to the p-type layer and the addition of the Group V atom of the periodic table to the n-type layer may each be in an amount of from 0.1 to 50 atom % as an optimum amount.

[0124] The hydrogen atoms (H,D) or halogen atoms (X) contained in the p-type layers or n-type layers also act to compensate unbonded arms in the p-type layer or n-type layer to improve the doping efficiency of the p-type layer or n-type layer. The hydrogen atoms or halogen atoms may be added to the p-type layer or n-type layer in an amount of from 0.1 to 40 atom % as an optimum amount. Especially when the p-type layer or n-type layer is crystalline, the hydrogen atoms or halogen atoms may be added in an amount of from 0.1 to 8 atom % as an optimum amount.

[0125] As a preferable form of distribution, the hydrogen atoms and/or halogen atoms may be distributed in a larger content on the side of the interfaces between p-type layer and i-type layer and between n-type layer and i-type layer. In the vicinity of the interfaces, the hydrogen atoms and/or halogen atoms may be contained in an amount 1.05 to 2 times their content in the bulk, as a preferable range.

[0126] When in this way the content of the hydrogen atoms or halogen atoms is made larger in the vicinity of the interfaces between p-type layer and i-type layer and between n-type layer and i-type layer, any defect levels and mechanical strain in the vicinity of the interfaces can be reduced and the photovoltaic effect and photoelectric currents of the stacked photovoltaic device of the present invention can be enhanced.

[0127] As electrical characteristics of the p-type layer or n-type layer of the photovoltaic device, the layer may preferably have an activation energy of 0.2 eV or below, and most preferably 0.1 eV or below. It may also preferably have a specific resistance of 100 Ω·cm or below, and most preferably 1 Ω·cm or below. The p-type layer or n-type layer may preferably have a layer thickness of from 1 nm to 50 nm, and most preferably from 3 nm to 10 nm.

[0128] (Formation of Semiconductor Layers)

[0129] The Group IV and Groups III-V alloy type amorphous semiconductor layers preferable as the semiconductor layers of the stacked photovoltaic device of the present invention may most preferably be formed by microwave plasma CVD or VHF (very high frequency) plasma CVD, and second preferably by RF (radio frequency) plasma CVD.

[0130] The microwave plasma CVD and VHF plasma CVD are processes in which material gases such as film-forming gases and dilute gases are fed into a deposition chamber (a vacuum chamber) that can be brought into a vacuum state, the internal pressure of the deposition chamber is kept constant while evacuating it by means of a vacuum pump, and microwaves or VHF waves generated by a microwave power source or a VHF power source are guided through a waveguide or a coaxial cable and introduced into the deposition chamber through a dielectric window (such as alumina ceramic window) or a conductor (a rod of Ni, W or stainless steel) electrically insulated from the deposition chamber, where plasma of the material gases is caused to take place to carry out decomposition, to thereby form desired deposited films on the substrate placed in the deposition chamber. Thus, deposited films applicable to photovoltaic devices can be formed under broad deposition conditions.

[0131] In the case where the semiconductor layers in the stacked photovoltaic device of the present invention are deposited by microwave plasma CVD or VHF plasma CVD, substrate temperature in the deposition chamber may preferably be set in the range of from 250 to 500° C.; internal pressure, from 0.5 to 250 mTorr; microwave power or VHF power, from 0.01 to 1 W/cm^3; and microwave frequency or VHF wave frequency, from 0.1 to 10 GHz.

[0132] In the case where they are deposited by RF plasma CVD, substrate temperature in the deposition chamber may preferably be set, as preferable conditions, in the range of from 100 to 350° C.; internal pressure, from 0.1 to 10 Torr; RF power, from 0.01 to 5.0 W/cm^3; and deposition rate, from 0.1 to 15 A/sec.

[0133] As a deposited-film forming method suited for the formation of the semiconductor layers in the stacked photovoltaic device of the present invention, a roll-to-roll system is available. In this deposited-film forming method, a plurality of glow-discharge regions are arranged along a path successively passing through them, and a belt-like substrate is transported continuously in the longitudinal direction while depositing and forming thereon semiconductor layers with necessary conductivity types in the respective glow-discharge regions. Thus, photovoltaic devices having the desired semiconductor junctions can be formed continuously.

[0134] The material gases suited for depositing the Groups IV-IV and Groups III-V alloy type amorphous semiconductor layers preferable in the stacked photovoltaic device of the present invention may include gasifiable compounds containing silicon atoms, gasifiable compounds containing germanium atoms, gasifiable compounds containing carbon atoms, gasifiable compounds containing nitrogen atoms, gasifiable compounds containing oxygen atoms, and mixed gases of any of these compounds.

[0135] Stated specifically, as the gasifiable compounds containing silicon atoms, chain or cyclic silane compounds may be used, specifically including, e.g., gaseous or readily gasifiable compounds such as SiH_4, Si_2H_6, SiF_4, $SiFH_3$, SiF_2H_2, SiF_3H, Si_3H_8, SiD_4, $SiHD_{37}$ SiH_2D_2, SiH_3D, $SiFD_3$, SiF_2D_2, $Si_2D_3H_3$, $(SiF_2)_5$, $(SiF_2)_6$, $(SiF_2)_4$, Si_ZF_6, S_3F_8, $Si_2H_2F_4$, $Si_2H_3F_3$, $SiCl_4$, $(SiCl_2)_5$, $SiBr_4$, $(SiBr_2)_5$, Si_2Cl_6, $SiHCl_3$, SiH_2Br_2, SiH_2Cl_2 and $Si_2Cl_3F_3$.

[0136] The gasifiable compounds containing germanium atoms may specifically include GeH_4, GeD_4, GeF_4, $GeFH_3$, GeF_2H_2, GeF_3H, $GeHD_3$, GeH_2D_2, GeH_3D, Ge_2H_6 and Ge_2D_6.

[0137] The gasifiable compounds containing carbon atoms may specifically include CH_4, CD_4, C_nH_{2n+2} (n is an integer), C_nH_{2n} (n is an integer), C2H_2, C_6H_6, C and CO.

[0138] The nitrogen-containing compounds may include N_2, NH_3, ND_3, NO, NO_z and N_2O.

[0139] The oxygen-containing compounds may include O_2, CO, CO_2, NO, NO_2, N_2O, CH_3CH_2OH and CH_3OH.

[0140] Materials incorporated into the p-type layer or n-type layer in order to control valence electrons may include Group III atoms and Group V atoms of the periodic table.

[0141] Materials effectively used as starting materials for incorporating Group III atoms may specifically include, as those for incorporating boron atoms, boron hydrides such as B_2H_6, B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12} and B_6H_{14}, and boron halides such as BF_3 and BCl_3. Besides, the materials may also include $AlCl_3$, $GaCl_3$, $InCl_3$ and $TlCl_3$. B_2H_6 and BF_3 are particularly suited.

[0142] Materials effectively used as starting materials for incorporating Group V atoms may specifically include, as those for incorporating phosphorus atoms, phosphorus hydrides such as PR_3 and P_2H_4 and phosphorus halides such as PH_4I, PF_3, PF_5, PCl_3, PCl_5, PBr_3, PBr_5 and PI_3. Besides, the materials may also include AsH_3, AsF_3, $AsCl_3$, $AsBr_3$, AsF_5, SbH_3, SbF_3, SbF_5, $SbCl_3$, $SbCl_5$, BiH_3, $BiCl_3$ and $BiBr_3$. PH_3 and PF_3 are particularly suited.

[0143] These gasifiable compounds may be fed into the deposition chamber after they are appropriately diluted with a gas such as H_2, He, Ne, Ar, Xe or Kr.

[0144] Especially when the layers having less optical absorbance or a broad band gap, such as microcrystalline semiconductor layers and a-SiC:H layers are deposited, the material gases may preferably be diluted to 1/2 to 1/100 with hydrogen gas, followed by feeding of microwave power or RF power which may be a relatively high power.

[0145] (Transparent Electrode)

[0146] In the present invention, the transparent electrode **115** is a light-transmitting electrode provided on the light-incident side, and also serves as a reflection preventive film when controlled to have an optimum layer thickness. The transparent electrode **115** is required to have a high transmittance in a wavelength region where the semiconductor layers can absorb light, and to have a low resistivity. It may preferably have a transmittance of 80% or above, and more preferably 85% or above, at 550 nm.

[0147] The transparent electrode may also preferably have a resistivity of 5×10^{-3} Ω·cm or below, and more preferably 1×10^{-3} Ω·cm or below.

[0148] As materials for the transparent electrode, conductive oxides such as In_2O_3, SnO_2, ITO (In_2O_3+SnO_2), ZnO, CdO, Cd_2SnO_4, TiO_2, Ta_2O_5, Bi_2O_3, MoO_3 and Na_xWO_3 or a mixture of some of these are preferably used.

[0149] An element capable of changing conductivity (i.e., a dopant) may also be added to these compounds. As the element capable of changing conductivity (a dopant), Al, In, B, Ga, Si and F may preferably be used in the case where the transparent electrode **115** is formed of ZnO; Sn, F, Te, Ti, Sb and Pb, when formed of In_2O_3; and F, Sb, P, As, In, Tl, Te, W, Cl, Br and I, when formed of SnO_2.

[0150] As methods for forming the transparent electrode, vapor deposition, CVD, spraying, spin-on processing and dipping may preferably be used.

[0151] (Collector Electrode)

[0152] In the present invention, the collector electrode **116** is provided optionally on part of the transparent electrode **115** when the transparent electrode **115** can not be made to have a sufficiently low resistivity, and acts to lower the resistivity of the electrode and lower the series resistance of the photovoltaic device.

[0153] Materials for the collector electrode may include gold, silver, copper, aluminum, nickel, iron, chromium, molybdenum, tungsten, titanium, cobalt, tantalum, niobium and zirconium, alloys such as stainless steel, and conductive pastes making use of powdery metals. As the shape thereof, the electrode is formed in a comb so that the light incident on the semiconductor layers is not intercepted as far as possible.

[0154] In the whole area of the photovoltaic device, the collector electrode may preferably cover an area of not more than 15%, more preferably not more than 10%, and most preferably not more than 5%.

[0155] The pattern of the collector electrode may be formed using a mask and, as methods therefor, by vapor deposition, sputtering, plating or printing. A wire-like metal may also be stuck with a conductive paste.

[0156] When a photovoltaic apparatus having the desired output voltage and output current is manufactured using the stacked photovoltaic device of the present invention, a plurality of stacked photovoltaic devices of the present invention are connected in series or in parallel, protective films are formed on the top surface and the back surface, and electrodes for collecting outputs are attached. In the case where the stacked photovoltaic devices of the present invention are connected in series, diodes for preventing back currents are incorporated in some cases.

EXAMPLES

[0157] The present invention will be described below by giving preferred examples. The present invention is by no means limited to these examples.

Example 1

[0158] The stacked photovoltaic device as shown in **FIG. 1** was produced using a deposition system shown in **FIG. 4**. A deposition system **400** can carry out all of MWPCVD (microwave plasma CVD), VHFPCVD (VHF plasma CVD) and RFPCVD (radio frequency plasma CVD). Using this deposition system **400**, the respective semiconductor layers were formed on a substrate **490** having light-reflecting layers **101** and **102**.

[0159] To the deposition system, material gas cylinders (not shown) are connected through gas feed pipes. The material gas cylinders contain all purified gases in an ultra-high purity, and an SiH_4 gas cylinder, a CH_4 gas cylinder, a GeH_4 gas cylinder, an Si_2H_6 gas cylinder, a PH_3/H_2 (dilution: 2.0%) gas cylinder, a B_2H_6/H_2 (dilution: 2.0%) gas cylinder, an H_2 gas cylinder, an He gas cylinder, an $SiCl_2H_2$ gas cylinder and an SiH_4/H_2 (dilution: 2%) gas cylinder were connected.

[0160] Next, the substrate **490**, on which a metal layer **101** and a transparent conductive layer **102** had been formed, was placed on a substrate transporting rail **413** provided in a load chamber **401**, and the inside of the load chamber **401** was evacuated by means of a vacuum exhaust pump (not shown) to have a pressure of about 1×10^{-5} Torr.

[0161] Next, a gate valve **406** was opened to carry the substrate into a transport chamber **402** evacuated previously by means of a vacuum exhaust pump (not shown) and then into a deposition chamber **417**. The substrate **490** was heated

in the manner the back surface thereof was brought into close contact with a substrate heater **410**. Then, the inside of the deposition chamber **417** was evacuated by means of a vacuum exhaust pump (not shown) to have a pressure of about 1×10^{-5} Torr.

[**0162**] After it was completed to make film formation ready as described above, H_2 gas was fed into the deposition chamber **417** through a gas feed pipe **429**. Then, valves **441**, **431** and **430** were opened, and H_2 gas flow rate was controlled by means of a mass flow controller **436** so as to be 300 sccm. The pressure inside the deposition chamber **417** was controlled by means of a conductance valve (not shown) so as to be 1.0 Torr. The substrate heater **410** was set so as to bring the temperature of the substrate **490** to 350° C. a At the time the substrate temperature became stable, a third p-i-n, RF n-type layer **103** comprised of μc-Si was formed.

[**0163**] To form the third p-i-n, RF n-type layer **103** comprised of μc-Si, valves **443**, **433**, **444** and **434** were operated to feed SiH_4 gas and PH_3/H_2 gas into the deposition chamber **417** through the gas feed pipe **429**.

[**0164**] Here, SiH_4 gas flow rate, H_2 gas flow rate and PH_3/H_2 gas flow rate were controlled by means of mass flow controllers **438**, **436** and **439** so as to be 0.4 sccm, 90 sccm and 0.5 sccm, respectively, and the pressure inside the deposition chamber **417** was controlled so as to be 1.0 Torr.

[**0165**] Power of the high-frequency (hereinafter "RF") power source **422** was set to 0.55 W/cm^3, and RF power was fed to a plasma forming cup **420** to cause glow discharge to take place. Thus, the third p-i-n, RF n-type layer was started being formed on the substrate, and a third p-i-n, RF n-type layer with a layer thickness of 10 nm was formed, whereupon the RF power source was turned off to stop the glow discharge to complete the formation of the third p-i-n, RF n-type layer **103**. The SiH_4 gas, PH_3/H_2 gas and H_2 gas were stopped from flowing into the deposition chamber **417**, and then the inside of the deposition chamber and the inside of the gas pipe were evacuated to have a pressure of 1×10^{-5} Torr.

[**0166**] Next, a third p-i-n, MW i-type layer **105** comprised of μc-Si and a third p-i-n, RF i-type layer **106** comprised of a-Si were formed successively in the following way.

[**0167**] First, a gate valve **407** was opened to carry the substrate **490** (with the above layer formed thereon) into a transport chamber **403** and an i-type layer deposition chamber **418** which were evacuated previously by means of a vacuum exhaust pump (not shown). Incidentally, an enlarged view of the inside of the i-type layer deposition chamber **418** is shown in a circle in **FIG. 4**. The substrate **490** was heated in the manner the back surface thereof was brought into close contact with a substrate heater **411**. Then, the inside of the i-type layer deposition chamber **418** was evacuated by means of a vacuum exhaust pump (not shown) to have a pressure of about 1×10^{-5} Torr.

[**0168**] To form the third p-i-n, MW i-type layer **105**, the substrate heater **411** was set so as to bring the temperature of the substrate **490** to 300° C. At the time the substrate was heated well, valves **461**, **451**, **450**, **463** and **453** were opened slowly to flow SiH_4 gas and H_2 gas into the i-type layer deposition chamber **418** through a gas feed pipe **449**.

[**0169**] Here, SiH_4 gas flow rate and H_2 gas flow rate were controlled by means of corresponding mass flow controllers **456** and **458** so as to be 80 sccm and 2,400 sccm, respectively. The pressure inside the i-type layer deposition chamber **418** was controlled so as to be 50 mTorr by adjusting the opening of a conductance valve (not shown). The power of an RF power source **424** was set to 0.22 W/cm^3, and was applied to a bias rod **428**.

[**0170**] Thereafter, the power of a microwave power source (2.45 GHz) (not shown) was set to 0.12 W/cm^3, and the microwave power was fed into the i-type layer deposition chamber **418** through a waveguide **426** and a microwave introducing window **425** to cause glow discharge to take place, and a shutter **427** was opened. Thus, the third p-i-n, MW i-type layer was started being formed on the third p-i-n, RF n-type layer, and an i-type layer with a layer thickness of 3.0 μm was formed, whereupon the microwave glow discharge was stopped and the output from the bias power source **424** was stopped to complete the formation of the third p-i-n, MW i-type layer **105**.

[**0171**] The valves **451** and **453** were closed to stop the SiH_4 gas and H_2 gas from flowing into the i-type layer deposition chamber **418**, and then the inside of the i-type layer deposition chamber **418** and the inside of the gas pipe were evacuated to have a pressure of 1×10^{-5} Torr.

[**0172**] To form the third p-i-n, RF i-type layer **106**, the substrate heater **411** was set so as to bring the temperature of the substrate **490** to 300° C. At the time the substrate was heated well, valves **464**, **454**, **450**, **463** and **453** were opened slowly to flow Si_2H_6 gas and H_2 gas into the i-type layer deposition chamber **418** through the gas feed pipe **449**.

[**0173**] Here, Si_2H_6 gas flow rate and H_2 gas flow rate were controlled by means of corresponding mass flow controllers **459** and **458** so as to be 3.8 sccm and 100 sccm, respectively. The pressure inside the i-type layer deposition chamber **418** was controlled so as to be 0.8 Torr by adjusting the opening of a conductance valve (not shown).

[**0174**] Next, the power of the RF power source **424** was set to 0.0088 W/cm^3 and was applied to the bias rod **428** to cause glow discharge to take place, and the shutter **427** was opened. Thus, the third p-i-n, RF i-type layer was started being formed on the third p-i-n, MW i-type layer, and an i-type layer with a layer thickness of 23 nm was formed, whereupon the RF glow discharge was stopped and the output from the RF power source **424** was stopped to complete the formation of the third p-i-n, RF i-type layer **106**.

[**0175**] The valves **464**, **454**, **453** and **450** were closed to stop the Si_2H_6 gas and H_2 gas from flowing into the i-type layer deposition chamber **418**, and then the inside of the i-type layer deposition chamber **418** and the inside of the gas pipe were evacuated to have a pressure of 1×10^{-5} Torr.

[**0176**] To form a third p-i-n, RF p-type layer **107** comprised of SiC, a gate valve **408** was opened to carry the substrate **490** (with the above layers formed thereon) into a transport chamber **404** and a p-type layer deposition chamber **419** which were evacuated previously by means of a vacuum exhaust pump (not shown). The substrate **490** was heated in the manner the back surface thereof was brought into close contact with the substrate heater **412**. Then, the inside of the p-type layer deposition chamber **419** was

evacuated by means of the vacuum exhaust pump (not shown) to have a pressure of about 1×10^{-5} Torr.

[0177] The substrate heater **412** was set so as to bring the temperature of the substrate **490** to 300° C. At the time the substrate temperature became stable, valves **481, 471, 470, 482, 472, 483, 473, 484** and **474** were operated to feed H_2 gas, SiH_4/H_2 gas, B_2H_6/H_2 gas and CH_4 gas into the deposition chamber **419** through a gas feed pipe **469**.

[0178] Here, H_2 gas flow rate, SiH_4/H_2 gas flow rate, B_2H_6/H_2 gas flow rate and CH_4 gas flow rate were controlled by means of mass flow controllers **476, 477, 478** and **479** so as to be 75 sccm, 3 sccm, 9 sccm and 0.1 sccm, respectively, and the pressure inside the deposition chamber **419** was controlled so as to be 1.8 Torr by adjusting the opening of a conductance valve (not shown).

[0179] Next, the power of the RF power source **423** was set to 0.09 W/cm^3, and RF power was fed to a plasma forming cup 421 to cause glow discharge to take place. Thus, the third p-i-n, RF p-type layer was started being formed on the i-type layer, and an RF p-type layer with a layer thickness of 10 nm was formed, whereupon the RF power source was turned off to stop the glow discharge to complete the formation of the third p-i-n, RF p-type layer **107**.

[0180] The valves **472, 482, 473, 483, 474, 484, 471, 481** and **470** were closed to stop the SiH_4/H_2 gas, B_2H_6/H_2 gas, CH_4 gas and H_2 gas from flowing into the p-type layer deposition chamber **419**, and then the inside of the p-type layer deposition chamber **419** and the inside of the gas pipe were evacuated to have a pressure of 1×10^{-5} Torr.

[0181] To form a second p-i-n, RF n-type layer **108** comprised of μc-Si, first the gate valve **408** was opened to carry the substrate **490** (with the above layers formed thereon) into the transport chamber **403** and i-type layer deposition chamber **418** evacuated previously by means of a vacuum exhaust pump (not shown), and the gate valve **407** was also opened to carry the substrate **490** into the transport chamber **402** and n-type layer deposition chamber **417** evacuated previously by means of a vacuum exhaust pump (not shown).

[0182] The substrate **490** was heated in the manner the back surface thereof was brought into close contact with the substrate heater **410**. Then, the inside of the n-type layer deposition chamber **417** was evacuated by means of a vacuum exhaust pump (not shown) to have a pressure of about 1×10^{-5} Torr. The substrate heater **410** was set so as to bring the temperature of the substrate **490** to 320° C. At the time the substrate temperature became stable, the valves **443, 433, 444** and **434** were operated to feed SiH_4 gas and PH_3/H_2 gas into the deposition chamber **417** through the gas feed pipe **429**.

[0183] Here, SiH_4 gas flow rate, H_2 gas flow rate and PH_3/H_2 gas flow rate were controlled by means of the mass flow controllers **438, 436** and **439** so as to be 0.6 sccm, 150 sccm and 3 sccm, respectively, and the pressure inside the deposition chamber **417** was controlled so as to be 1.2 Torr.

[0184] Next, the power of the RF power source **422** was set to 0.07 W/cM^3, and RF power was fed to the plasma forming cup **420** to cause glow discharge to take place. Thus, the second p-i-n, RF n-type layer was started being formed on the third p-i-n, RF p-type layer, and a second p-i-n, RF n-type layer with a layer thickness of 100 nm was formed, whereupon the RF power source was turned off to stop the glow discharge to complete the formation of the second p-i-n, RF n-type layer **108**.

[0185] The SiH_4 gas, PH_3/H_2 gas and H_2 gas were stopped from flowing into the deposition chamber 417, and then the inside of the deposition chamber and the inside of the gas pipe were evacuated to have a pressure of 1×10^{-5} Torr.

[0186] To form a second p-i-n, i-type layer **110** comprised of μc-Si, the gate valve **407** was opened to carry the substrate **490** (with the above layers formed thereon) into the transport chamber **403** and i-type layer deposition chamber **418** evacuated previously by means of a vacuum exhaust pump (not shown).

[0187] The substrate heater **411** was set so as to bring the temperature of the substrate **490** to 290° C. At the time the substrate was heated well, the valves **461, 451, 450, 463** and **453** were opened slowly to flow SiH_4 gas and H_2 gas into the i-type layer deposition chamber **418** through the gas feed pipe **449**.

[0188] Here, SiH_4 gas flow rate and H_2 gas flow rate were controlled by means of the corresponding mass flow controllers **456** and **458** so as to be 45 sccm and 1,500 sccm, respectively. The pressure inside the i-type layer deposition chamber **418** was controlled so as to be 0.04 Torr by adjusting the opening of the conductance valve (not shown).

[0189] Next, the power of the RF power source **424** was set to 0.15 W/cm^3, and was applied to the bias rod **428**. Thereafter, the power of a microwave power source (not shown; 0.5 GHz) was set to 0.10 W/cm^3, and the microwave power was fed into the i-type layer deposition chamber **418** through the bias rod **428** to cause glow discharge to take place. Thus, the second p-i-n, i-type layer was started being formed on the second p-i-n, RF n-type layer, and a layer with a layer thickness of 0.8 μm was formed, whereupon the glow discharge was stopped and the output from the bias power source 424 was stopped to complete the formation of the second p-i-n, i-type layer **110**.

[0190] The valves **451** and **453** were closed to stop the SiH_4 gas and H_2 gas from flowing into the i-type layer deposition chamber **418**, and then the inside of the i-type layer deposition chamber **418** and the inside of the gas pipe were evacuated to have a pressure of 1×10^{-5} Torr.

[0191] To form a second p-i-n, RF p-type layer **111** comprised of SiC, the substrate **490** (with the above layers formed thereon) was carried in the same manner as the formation of the third p-i-n, RF p-type layer **107**. The subsequent procedure for the third p-i-n, RF p-type layer was repeated except that the H_2 gas flow rate, SiH_4/H_2 gas flow rate, B_2H_6/H_2 gas flow rate and CH_4 gas flow rate were controlled by means of the mass flow controllers so as to be 80 sccm, 3 sccm, 9 sccm and 0.2 sccm, respectively, and the deposition was carried out at a substrate temperature of 260° C.

[0192] To form a first p-i-n, RF n-type layer **112** comprised of a-Si, firstly the gate valve **408** was opened to carry the substrate **490** (with the above layers formed thereon) into the transport chamber **403** and i-type layer deposition chamber **418** evacuated previously by means of a vacuum exhaust

pump (not shown), and also the gate valve **407** was opened to carry the substrate **490** into the transport chamber **402** and n-type layer deposition chamber **417** evacuated previously by means of a vacuum exhaust pump (not shown).

[**0193**] SiH_4 gas flow rate, H_2 gas flow rate and PH_3/H_2 gas flow rate were controlled by means of the mass flow controllers **438**, **436** and **439** so as to be 1.1 sccm, 45 sccm and 9 sccm, respectively, and the pressure inside the deposition chamber **417** was controlled by means of a conductance valve (not shown) so as to be 1.05 Torr.

[**0194**] The substrate heater **410** was set so as to bring the temperature of the substrate **490** to 230° C. At the time the substrate temperature became stable, the first p-i-n, RF n-type layer **112** comprised of a-Si was formed.

[**0195**] To form a first p-i-n, RF i-type layer **113** comprised of a-Si, the substrate **490** (with the above lo **1** layers formed thereon) was carried in the same manner as the formation of the third p-i-n, RF i-type layer **104**. Thereafter, the substrate temperature was set to 195° C., the Si_2H_6 gas flow rate and H_2 gas flow rate were controlled by means of the mass flow controllers **464** and **463** so as to be 2 sccm and 200 sccm, respectively, and the pressure inside the deposition chamber **417** was controlled so as to be 0.75 Torr. At an RF power set at 0.007 W/cm^3, a first p-i-n, RF i-type layer **113** with a layer thickness of 0.1 μm was formed.

[**0196**] To form a first p-i-n, RF p-type layer **114** comprised of SiC, the substrate **490** (with the above layers formed thereon) was carried in the same manner as the formation of the third p-i-n, RF p-type layer **107**. The subsequent procedure for the third p-i-n, RF p-type layer was repeated except that the H_2 gas flow rate, SiH_4/H_2 gas flow rate, B_2H_6/H_2 gas flow rate and CH_4 gas flow rate were controlled by means of the mass flow controllers so as to be 90 sccm, 3 sccm, 8 sccm and 0.4 sccm, respectively, and the deposition was carries out at a substrate temperature of 170° C.

[**0197**] Next, a gate valve **409** was opened to carry the substrate **490** (with the above layers formed thereon) into an unload chamber **405** evacuated previously by means of a vacuum exhaust pump (not shown), and a leak valve (not shown) was opened to let gases escape from the unload chamber **405**.

[**0198**] Next, on the first p-i-n, RF p-type layer **114**, ITO was deposited by vacuum vapor deposition in a layer thickness of 70 nm as the transparent electrode **115**.

[**0199**] Next, on the transparent electrode **115**, a mask with a comb-shaped opening was placed, and a comb-shaped collector electrode **116** comprised of Cr(40 nm)/Ag(1,000 nm)/Cr(40 nm) was deposited by vapor deposition.

[**0200**] Thus, the fabrication of the photovoltaic device of the present Example was completed. This photovoltaic device is herein called SCEx-**1**.

Comparative Example 1

[**0201**] In Example 1, the third p-i-n, n-type layer was formed to be comprised of a-Si; the third p-i-n, i-type layer, a-SiGe; the second p-i-n, n-type layer, μc-Si; and the second p-i-n, i-type layer, a-Si; which were all formed using RF power to produce a stacked photovoltaic device. This stacked photovoltaic device is herein called SCCp-**1**. The p-type, i-type and n-type layers other than the above were formed in the same manner as in Example 1.

[**0202**] Gas flow rates and other conditions are shown in Table 11.

[**0203**] For each of SCEx-**1** and SCCp-**1**, five samples were prepared, and their loss of efficiency with respect to initial efficiency under irradiation by light of AM 1.5 (100 mW/cm^2) at 45° C. for 3,000 hours (hereinafter simply "rate of deterioration by light"), photoelectric conversion efficiency after stabilization (stabilized conversion efficiency), efficiency after leaving in the dark at a temperature of 85° C. and a humidity of 85% RH for 2,100 hours (hereinafter simply "rate of heat-resistance deterioration"), cell breakdown voltage, and yield were measured.

[**0204**] The initial photoelectric conversion efficiency and stabilized conversion efficiency are determined by setting the resultant photovoltaic devices under irradiation by light of AM 1.5 (100 mW/cm^2) to measure V-I characteristics. As the result of measurement, the characteristics of SCCp-**1** on the basis of those of SCEx-**1** assumed as 1 were as shown in Table 1.

[**0205**] As can be seen from the foregoing, the stacked photovoltaic device SCEx-**1** of the present invention is superior to the conventional stacked photovoltaic device SCCp-**1** in stabilized conversion efficiency, rate of deterioration by light, rate of heat-resistance deterioration, cell breakdown voltage and yield.

Example 2

[**0206**] A photovoltaic device was produced in the same manner as in Example 1 except that the third p-i-n, i-type layer **105** comprised of μc-Si was formed by using VHF waves of 0.1 GHz in place of the microwaves.

[**0207**] The substrate heater **411** was set so as to bring the temperature of the substrate **490** to 330° C. At the time the substrate was heated well, the valves **461**, **451**, **450**, **463** and **453** were opened slowly to flow SiH_4 gas and H_2 gas into the i-type layer deposition chamber **418** through the gas feed pipe **449**.

[**0208**] Here, SiH_4 gas flow rate and H_2 gas flow rate were controlled by means of the corresponding mass flow controllers **456** and **458** so as to be 60 sccm and 2,400 sccm, respectively. The pressure inside the i-type layer deposition chamber **418** was controlled so as to be 0.2 Torr by adjusting the opening of the conductance valve (not shown).

[**0209**] Next, the power of a VHF power source (not shown; 0.1 GHz) was set to 0.15 W/cm^3, and was applied to the bias rod **428** to cause glow discharge to take place. Thus, the third p-i-n, i-type layer was started being formed on the third p-i-n, RF n-type layer, and an i-type with a layer thickness of 2.5 μm was formed, whereupon the glow discharge was stopped to complete the formation of the third p-i-n, i-type layer **105**.

[**0210**] The valves **451** and **453** were closed to stop the SiH_4 gas and H_2 gas from flowing into the i-type layer deposition chamber **418**, and then the inside of the i-type layer deposition chamber **418** and the inside of the gas pipe were evacuated to have a pressure of 1×10^{-5} Torr.

[**0211**] The stacked photovoltaic device thus obtained is called SCEx-**2**.

Comparative Example 2

[0212] In Example 1, the third p-i-n, n-type layer was formed to be comprised of a-Si; the third p-i-n, i-type layer, a-SiGe; the second p-i-n, n-type layer, a-Si; and the second p-i-n, i-type layer, a-SiGe; which were all formed using RF power to produce a stacked photovoltaic device. This stacked photovoltaic device is herein called SCCp-**2**. The p-type, i-type and n-type layers other than the above were formed in the same manner as in Example 1.

[0213] Gas flow rates and other conditions are shown in Table 21.

[0214] For each of SCEx-**2** and SCCp-**2**, four samples were prepared. Their photoelectric conversion efficiency after stabilization (stabilized conversion efficiency), rate of deterioration by light, rate of heat-resistance deterioration, cell breakdown voltage, and yield were measured, and their average values were calculated.

[0215] As the result of measurement, the characteristics of SCCp-**2** on the basis of those of SCEx-**2** assumed as 1 were as shown in Table 2.

[0216] As can be seen from the foregoing, the stacked photovoltaic device SCEx-**2** of the present invention is superior to the conventional stacked photovoltaic device SCCp-**2** in photoelectric conversion efficiency after stabilization (stabilized conversion efficiency), rate of deterioration by light, rate of heat-resistance deterioration, cell breakdown voltage and yield.

Example 3

[0217] In Example 1, to form the second p-i-n, i-type layer **110** comprised of μc-Si, SiH_4 gas flow rate and H_2 gas flow rate were controlled by means of the corresponding mass flow controllers **456** and **458** so as to be 70 sccm and 2,100 sccm, respectively. The pressure inside the i-type layer deposition chamber **418** was controlled so as to be 0.05 Torr by adjusting the opening of the conductance valve (not shown).

[0218] Next, the power of the RF power source **424** was set to 0.15 W/cm^3, and was applied to the bias rod **428**. Thereafter, the power of a VHF power source (not shown; 0.5 GHz) was set to 0.12 W/cm^3, and VHF power was fed into the i-type layer deposition chamber **418** through the bias rod **428** to cause glow discharge to take place. Thus, the second p-i-n, i-type layer was started being formed on the second p-i-n, RF n-type layer, and an i-type with a layer thickness of 1.0 μm was formed, whereupon the glow discharge was stopped and the output from the bias power source **424** was stopped to complete the formation of the second p-i-n, i-type layer **110**.

[0219] In the same way, eight samples were prepared in which only the layer thickness of the second p-i-n, i-type layer **110** comprised of μc-Si was changed in the range of from 0.3 μm to 2.0 μm, and their initial photoelectric conversion efficiency, fill factor, and rate of deterioration by light were measured.

[0220] Results obtained are shown in Table 3.

[0221] In respect of the initial photoelectric conversion efficiency, fill factor and rate of deterioration by light, those sufficient for practical use were obtained when the i-type layer **110** was formed in a layer thickness ranging from 0.5 μm to 1.5 μm.

[0222] In the stacked photovoltaic device of the present invention, those having superior characteristics were obtained when the second p-i-n, i-type layer **110** comprised of μc-Si was formed in a layer thickness ranging from 0.5 μm to 1.5 μm.

Example 4

[0223] In Example 1, to form the third p-i-n, i-type layer **105** comprised of μc-Si, SiH_4 gas flow rate and H_2 gas flow rate were controlled by means of the corresponding mass flow controllers **456** and **458** so as to be 80 sccm and 3,200 sccm, respectively. The pressure inside the i-type layer deposition chamber 418 was controlled so as to be 0.2 Torr by adjusting the opening of the conductance valve (not shown).

[0224] Next, the power of a VHF power source (not shown; 0.1 GHz) was set to 0.15 W/cm^3, and VHF power was fed into the i-type layer deposition chamber **418** through the bias rod **428** to cause glow discharge to take place. Thus, the third p-i-n, i-type layer was started being formed on the third p-i-n, RF n-type layer, and an i-type with a layer thickness of 3.0 μm was formed, whereupon the glow discharge was stopped and the output from the bias power source **424** was stopped to complete the formation of the third p-i-n, i-type layer **105**.

[0225] In the same way, eight samples were prepared in which only the layer thickness of the third p-i-n, i-type layer **105** comprised of μc-Si was changed in the range of from 1.0 μm to 4.0 μm, and their initial photoelectric conversion efficiency, fill factor, and rate of deterioration by light were measured.

[0226] Results obtained are shown in Table 4.

[0227] In respect of the initial photoelectric conversion efficiency, fill factor and rate of deterioration by light, those sufficient for practical use were obtained when the i-type layer **105** was formed in a layer thickness ranging from 1.5 μm to 3.5 μm.

[0228] In the stacked photovoltaic device of the present invention, those having superior characteristics were obtained when the third p-i-n, i-type layer **105** comprised of μc-Si was formed in a layer thickness ranging from 1.5 μm to 3.5 μm.

Example 5

[0229] In Example 1, the second p-i-n, n-type layer **108** was formed in the same way. To form the second p-i-n, i-type layer **110** comprised of μc-Si, SiH_4 gas flow rate and H_2 gas flow rate were controlled by means of the corresponding mass flow controllers **456** and **458** so as to be 55 sccm and 1,500 sccm, respectively, and also B_2H_6/H_2 gas flow rate was controlled by means of the mass flow controller **460** so that boron content in microcrystalline silicon of the second p-i-n, i-type layer **110** ranged from 0 ppm to 10.0 ppm, thus photovoltaic devices were produced. The n-type, i-type and p-type layers other than the above were formed in the same manner as in Example 1.

[0230] The boron content in the second p-i-n, i-type layer **110** was measured using IMF-4F, manufactured by Cameca Co.

[0231] In those having the second p-i-n, i-type layer **110** in which the boron contained in silicon was in an mount of 8.0 ppm or less, superior characteristics were obtained in respect of all the initial photoelectric conversion efficiency, stabilized conversion efficiency, rate of deterioration by light and rate of heat-resistance deterioration.

[0232] Results obtained are shown in Table 5.

Example 6

[0233] In Example 1, the third p-i-n, n-type layer **103** was formed in the same way. To form the third p-i-n, i-type layer **105** comprised of μc-Si, SiH_4 gas flow rate and H_2 gas flow rate were controlled by means of the corresponding mass flow controllers **456** and **458** so as to be 45 sccm and 1,550 sccm, respectively, and also B_2H_6/H_2 gas flow rate was controlled by means of the mass flow controller **460** so that boron content in microcrystalline silicon of the third p-i-n, i-type layer **105** ranged from 0 ppm to 10.0 ppm, thus photovoltaic devices were produced. The n-type, i-type and p-type layers other than the above were formed in the same manner as in Example 1.

[0234] The boron content in the third p-i-n, i-type layer **105** was measured using IMF-4F, manufactured by Cameca Co.

[0235] In those having the third p-i-n, i-type layer **105** in which the boron contained in silicon was in an mount of 8.0 ppm or less, superior characteristics were obtained in respect of all the initial photoelectric conversion efficiency, stabilized conversion efficiency, rate of deterioration by light and rate of heat-resistance deterioration.

[0236] Results obtained are shown in Table 6.

Example 7

[0237] In Example 1, a photovoltaic device was produced in which a second p-i-n, RF n-type layer comprised of a-Si was provided additionally between the layers **107** and **108**. **FIG. 2** illustrates a cross-sectional structure of such a stacked photovoltaic device.

[0238] To form the second p-i-n, RF n-type layer comprised of a-Si, the valves **443**, **433**, **444** and **434** were operated to feed SiH_4 gas and PH_3/H_2 gas into the deposition chamber **417** through the gas feed pipe **429**.

[0239] Here, SiH_4 gas flow rate, H_2 gas flow rate and PH_3/H_2 gas flow rate were controlled by means of the mass flow controllers **438**, **436** and **439** so as to be 3 sccm, 80 sccm and 5 sccm, respectively, and the pressure inside the deposition chamber **417** was controlled so as to be 1.0 Torr.

[0240] The power of the RF power source **422** was set to 0.03 W/cm^3, and RF power was fed to the plasma forming cup **420** to cause glow discharge to take place. Thus, an RF n-type layer **208** was started being formed on the third p-i-n, p-type layer **207**, and the second p-i-n, RF n-type layer with a layer thickness of 10 nm was formed, whereupon the RF power source was turned off to stop the glow discharge to complete the formation of a second p-i-n, RF n-type layer **208**.

[0241] The SiH_4 gas, PH_3/H_2 gas and H_2 gas were stopped from flowing into the deposition chamber **417**, and then the inside of the deposition chamber and the inside of the gas pipe were evacuated to have a pressure of 10^{-5} Torr. An n-type layer **209** comprised of μc-Si was further formed in the same manner as in Example 1 in a layer thickness of 10 nm.

[0242] Other deposited layers were formed in the same manner as in Example 1 to obtain the stacked photovoltaic device as shown in **FIG. 2**. This photovoltaic device is herein called SCEx-**7**.

Comparative Example 7

[0243] In Example 1, the third p-i-n, n-type layer was formed to be comprised of a-Si; the third p-i-n, i-type layer, a-SiGe; the second p-i-n, n-type layer, a-Si; and the second p-i-n, i-type layer, a-Si; which were all formed using RF power to produce a stacked photovoltaic device. This photovoltaic device is herein called SCCp-**7**. The p-type, i-type and n-type layers other than the above were formed in the same manner as in Example 1.

[0244] Gas flow rates and other conditions are shown in Table 71.

[0245] For each of SCEx-**7** and SCCp-**7**, six samples were prepared. Their stabilized conversion efficiency, rate of deterioration by light, rate of heat-resistance deterioration, cell breakdown voltage, and yield were measured in the same manner as in Comparative Example 1, and their average values were calculated. As the result of measurement, the characteristics of SCCp-**7** on the basis of those of SCEx-**7** assumed as 1 were as shown in Table 7.

[0246] As can be seen from the foregoing, the stacked photovoltaic device SCEx-**7** of the present invention is superior to the conventional stacked photovoltaic device SCCp-**7** in stabilized conversion efficiency, rate of deterioration by light, rate of heat-resistance deterioration, cell breakdown voltage and yield.

Example 8

[0247] In the same manner as in Example 1 to form the μc-Si layer i-type layer **110** of the second p-i-n junction, the rate of dilution with hydrogen, substrate temperature and so forth were changed previously to study production conditions providing different optical absorption coefficients at 950 nm. Thereafter, four stacked photovoltaic devices having different optical absorption coefficients at 950 nm were produced by using the above production conditions when in Example 1 the μc-Si layer i-type layer 110 of the second p-i-n junction was formed. Then, evaluation was made in the same manner as in Example 1.

[0248] The results of evaluation are shown in Table 8.

[0249] As can be seen from the foregoing, the stacked photovoltaic device SCEx-**8** of the present invention has superior characteristics in respect of all the initial photoelectric conversion efficiency, stabilized conversion efficiency, rate of deterioration by light and rate of heat-resistance deterioration when its microcrystalline silicon i-type layer of the second p-i-n junction is made to have an optical absorption coefficient of 200 cm^{-1} or above at 950 nm.

Example 9

[0250] In the same manner as in Example 1 to form the μc-Si layer i-type layer **105** of the third p-i-n junction, the rate of dilution with hydrogen, substrate temperature and so forth were changed previously to study production conditions providing different optical absorption coefficients at 950 nm. Thereafter, four stacked photovoltaic devices having different optical absorption coefficients at 950 nm were produced by using the above production conditions when in Example 1 the μc-Si layer i-type layer **105** of the third p-i-n junction was formed. Then, evaluation was made in the same manner as in Example 1.

[0251] The results of evaluation are shown in Table 9.

[0252] As can be seen from the foregoing, the stacked photovoltaic device SCEx-**9** of the present invention has superior characteristics in respect of all the initial photoelectric conversion efficiency, stabilized conversion efficiency, rate of deterioration by light and rate of heat-resistance deterioration when its microcrystalline silicon i-type layer of the third p-i-n junction is made to have an optical absorption coefficient of 200 cm^{-1} or above at 950 nm.

Example 10

[0253] The triple type photovoltaic device as shown in **FIG. 3** was produced using a deposition system employing a roll-to-roll system as shown in **FIG. 5**. In **FIG. 5**, reference numeral **5010** denotes a load chamber; **5400**, a substrate wound up in a role in the load chamber; **5150**, an unload chamber; and **5402**, a wind-up jig provided in the unload chamber.

[0254] Reference numeral **5120** denotes a first p-i-n, n-type layer deposition chamber; **5130**, a first p-i-n, RF i-type layer (p/i) deposition chamber; and **5140**, a first p-i-n, p-type layer deposition chamber. Also, reference numeral **5070** denotes a deposition chamber for a second p-i-n, n-type layer; **5090**, a deposition chamber for a second p-i-n, MW i-type layer; and **5110**, a second p-i-n, p-type layer deposition chamber. Still also, reference numerals **5020** and **5030** denote third p-i-n, n-type layer deposition chambers; **5040**, a third p-i-n, MW i-type layer deposition chamber; **5050**, a third p-i-n, RF i-type layer (p/i) deposition chamber; and **5060**, a third p-i-n, p-type layer deposition chamber.

[0255] Reference numerals **5011, 5021, 5031, 5041, 5051, 5061, 5071, 5091, 5111, 5121, 5131, 5141** and **5151** denote exhaust pipes; and **5012, 5022, 5032, 5042, 5052, 5062, 5072, 5092, 5112, 5122, 5132, 5142** and **5152**, exhaust pumps connected to the exhaust pipes.

[0256] Reference numerals **5201** to **5214** denotes gas gates; and **5301** to **5314**, gas feed pipes. Also, reference numerals **5025, 5035, 5045, 5055, 5065, 5075, 5095, 5115, 5125, 5135** and **5145** denote material gas feed pipes; and **5026, 5036, 5046, 5056, 5066, 5076, 5096, 5116, 5126, 5136** and **5146**, material gas mixing systems.

[0257] Reference numerals **5024, 5034, 5054, 5064, 5074, 5114, 5124, 5134** and **5144** denote RF power sources; and **5023, 5033, 5053, 5063, 5073, 5113, 5123, 5133** and **5143**, coaxial cables for RF power supply. Also, reference numerals **5044** and **5094** denote MW power sources; and **5043** and **5093**, MW-introducing waveguides.

[0258] As the substrate, a sheet-like substrate of 300 m long, 30 cm wide and 0.2 mm thick having thereon a light reflecting layer (metal layer and transparent conductive layer) was used.

[0259] Then, the sheet-like substrate having the light-reflecting layer was set in the load chamber **5010** for feeding the substrate. Conditions for forming the triple type photovoltaic devices are shown in Table **101**.

[0260] The sheet-like substrate was passed through all the deposition chambers and all the gas gates and connected to the sheet wind-up jig in the unload chamber **5150**. The respective deposition chambers were evacuated to 10^{-3} Torr or below by means of exhaust systems (not shown). The desired materials gases were fed into the respective deposition chambers from the deposited film forming mixing systems **5026, 5036, 5046, 5056, 5066, 5076, 5096, 5116, 5126, 5136** and **5146**. To the gas gates **5201** to **5214**, gas was fed from the respective gate gas feeding system.

[0261] The substrate was heated by means of the substrate heater in each deposition system, and the degree of vacuum was controlled by adjusting the opening of the exhaust valve of each exhaust system. After the substrate temperature and degree of vacuum became stable, the substrate was started being transported, and RF power, VHF wave or microwave (frequency: 0.5 GHz, 2.45 GHz) power for generating plasma was supplied to each deposition chamber.

[0262] In this way, the triple type photovoltaic device having the three p-i-n junctions superposed as shown in **FIG. 3** was formed on the sheet-like substrate over a length of 100 m. In the formation of the second p-i-n, i-type layer, VHF waves (0.5 GHz) were applied. In the formation of the third p-i-n, i-type layer, microwaves (2.45 GHz) were applied.

[0263] Next, on the RF p-type layer **114**, ITO was deposited by vacuum vapor deposition in a layer thickness of 70 nm as the transparent electrode **115**.

[0264] Then, on the transparent electrode **115**, a mask with a comb-shaped opening was placed, and the comb-shaped collector electrode **116** comprised of Cr(40 nm)/Ag(1,000 nm)/Cr(40 nm) was deposited by vapor deposition. Thus, the fabrication of the stacked photovoltaic device was completed. This photovoltaic device is herein called SCEx-**10**.

Comparative Example 10

[0265] Under the same conditions as in Example 10, like Comparative Example 1, third p-i-n, RF n-type layer, i-type layer, MW i-type layer, RF i-type layer and p-type layer, second p-i-n, RF n-type layer, i-type layer and p-type layer, and first p-i-n, RF n-type layer, i-type layer and p-type layer were formed on the substrate having the reflecting layer, to produce a stacked photovoltaic device in which a-Si was used in the second p-i-n, RF n-type layer and a-Si was used in the second p-i-n, i-type layer.

[0266] For each of SCEx-**10** and SCCp-**10**, eight samples were prepared. Their stabilized conversion efficiency, rate of deterioration by light, rate of heat-resistance deterioration, cell breakdown voltage and yield were measured, and their average values were calculated. As the result of measurement, the characteristics of SCCp-**10** on the basis of those of SCEx-**10** assumed as 1 were as shown in Table 10.

[0267] As can be seen from the foregoing, the stacked photovoltaic device SCEx-**10** of the present invention is superior to the conventional stacked photovoltaic device SCCp-**10** in stabilized conversion efficiency, rate of deterioration by light, rate of heat-resistance deterioration, cell breakdown voltage and yield.

[0268] As described above, according to the present invention, the use of a microcrystalline silicon layer as the i-type layer of the second p-i-n junction and a microcrystalline silicon layer as the i-type layer of the third p-i-n junction brings about an improvement in semiconductor layers which have hitherto undergone a great deterioration by light in amorphous silicon type stacked photovoltaic devices, and especially makes it possible to more restrain the deterioration by light than any conventional stacked photovoltaic devices.

[0269] The use of a microcrystalline silicon layer as the i-type layer of the third p-i-n junction also makes it possible to absorb long-wavelength light which has hitherto been relatively difficult to absorb, to achieve higher short-circuit current and open circuit voltage than any conventional stacked photovoltaic devices, and also to maintain a high photoelectric conversion efficiency.

[0270] With regard to the layer thickness of the microcrystalline silicon layer which is the i-type layer of the second p-i-n junction and/or the layer thickness of the microcrystalline silicon layer which is the i-type layer of the third p-i-n junction, making it/them smaller beyond the layer thickness having hitherto been considered suitable make(s) it possible to restrain localized levels in the i-type layer from increasing as a result of irradiation by light, and especially to more restrain the deterioration by light than any conventional stacked photovoltaic devices.

[0271] Incorporation of boron in the microcrystalline silicon layer which is the i-type layer of the second p-i-n junction and setting its content to be not more than 8 ppm, and/or incorporation of boron in the microcrystalline silicon layer which is the i-type layer of the third p-i-n junction and setting its content to be not more than 8 ppm make(s) it possible not to inhibit the growth of microcrystals and to improve the movability of holes at the time of electricity generation by light to thereby maintain a high photoelectric conversion efficiency while restraining the deterioration by light.

[0272] Formation of the n-type layer of the second p-i-n junction by a microcrystalline silicon layer or by a double layer consisting of a microcrystalline silicon layer and an amorphous silicon layer and/or formation of the n-type layer of the third p-i-n junction by a microcrystalline silicon layer or by a double layer consisting of a microcrystalline silicon layer and an amorphous silicon layer make(s) it possible to form at a high deposition rate the microcrystalline silicon of the i-type layer formed on the n-type layer, to form good-quality microcrystalline silicon having less impurities and to maintain a high photoelectric conversion efficiency with less deterioration by light.

[0273] In addition, with regard to the microcrystalline silicon layers which are the i-type layers of the second and third p-i-n junctions, their formation by plasma CVD using a high frequency power of from 0.1 GHz to 10 GHz and making these layers each have an optical absorption coefficient of 200 cm^{-1} or above at 950 nm make it possible to form the microcrystalline silicon layers which are the i-type layers of the second and third p-i-n junctions, in a layer thickness smaller beyond the layer thickness having hitherto been considered suitable, to restrain localized levels in the i-type layer from increasing as a result of irradiation by light, and especially to more restrain the deterioration by light than any conventional stacked photovoltaic devices. This also makes it possible to absorb long-wavelength light which has hitherto been relatively difficult to absorb, and to achieve higher photoelectric conversion efficiency than any conventional stacked photovoltaic devices.

[0274] The formation of the stacked photovoltaic device of the present invention by the roll-to-roll system makes it possible to improve productivity very much.

[0275] Thus, the stacked photovoltaic device of the present invention makes it possible to restrain deterioration by light, to make deterioration by light less occur while maintaining a high photoelectric conversion efficiency and to improve the photoelectric conversion efficiency after deterioration by light. Hence, a stacked photovoltaic device can be provided which is practicable and low-cost and yet has a high reliability, and also has a high photoelectric conversion efficiency.

[0276] According to the present invention, the use of microcrystalline silicon in the i-type layer of the second p-i-n junction and microcrystalline silicon in the i-type layer of the third p-i-n junction also makes it possible to improve breakdown voltage, resistance to deterioration by heat and production process yield of the whole photovoltaic device, and to improve flexibility of the form in which the photovoltaic device is utilized.

TABLE 11

(Comparative Example 1)

	SiH_4 Flow rate (sccm)	Si_2H_6 Flow rate (sccm)	CH_4 Flow rate (sccm)	GeH_4 Flow rate (sccm)	H_2 Flow rate (sccm)	PH_3/H_2 Flow rate (sccm)	B_2H_6/H_2 Flow rate (sccm)	SiH_4/H_2 Flow rate (sccm)	Pressure (Torr)	MW power (W/cm^3)	RF power (W/cm^3)	Substrate temp. (° C.)	Layer thickness (nm)
RF n-type layer:	2.2	—	—	—	80	10	—	—	1.3	—	0.05	380	10
RF i-type layer:	—	3.5	—	—	100	—	—	—	0.65	—	0.008	300	10

TABLE 11-continued

(Comparative Example 1)

	SiH_4 Flow rate (sccm)	Si_2H_6 Flow rate (sccm)	CH_4 Flow rate (sccm)	GeH_4 Flow rate (sccm)	H_2 Flow rate (sccm)	PH_3/H_2 Flow rate (sccm)	B_2H_6/H_2 Flow rate (sccm)	SiH_4/H_2 Flow rate (sccm)	Pressure (Torr)	MW power (W/cm^3)	RF power (W/cm^3)	Substrate temp. (° C.)	Layer thickness (nm)
MW i-type layer:	48	—	—	51	170	—	—	—	0.01	0.1	0.32	380	170
RF i-type layer:	—	3.5	—	—	100	—	—	—	0.65	—	0.008	300	23
RF p-type layer:	—	—	0.1	—	80	—	9	3	1.8	—	0.07	300	10
RF n-type layer:	0.5	—	—	—	100	8	—	—	1.2	—	0.1	320	10
MW i-type layer:	80	—	—	—	250	—	—	—	0.02	0.1	0.205	320	350
RF p-type layer:	—	—	0.2	—	80	—	9	3	1.7	—	0.07	260	10
RF n-type layer:	1.1	—	—	—	50	10	—	—	1.05	—	0.04	230	10
RF i-type layer:	—	2.0	—	—	200	—	—	—	0.8	—	0.007	190	90
RF p-type layer:	—	—	0.4	—	90	—	8	3	1.6	—	0.07	170	10

[0277]

TABLE 1

Sample	Stabilized conversion efficiency	Rate of deterioration by light	Rate of heat-resistance deterioration	Cell breakdown voltage	Yield
SCEx-1	1	1	1	1	1
SCCp-1	0.9	1.18	1.14	0.99	0.98

[0278]

TABLE 21

(Comparative Example 2)

	SiH_4 Flow rate (sccm)	Si_2H_6 Flow rate (sccm)	CH_4 Flow rate (sccm)	GeH_4 Flow rate (sccm)	H_2 Flow rate (sccm)	PH_3/H_2 Flow rate (sccm)	B_2H_6/H_2 Flow rate (sccm)	SiH_4/H_2 Flow rate (sccm)	Pressure (Torr)	MW power (W/cm^3)	RF power (W/cm^3)	Substrate temp. (° C.)	Layer thickness (nm)
RF n-type layer:	2.2	—	—	—	80	10	—	—	1.3	—	0.05	370	10
RF i-type	—	3.5	—	—	90	—	—	—	0.65	—	0.008	300	10
MW i-type layer:	48	—	—	53	170	—	—	—	0.02	0.1	0.32	370	170
RF i-type layer:	—	3.5	—	—	90	—	—	—	0.67	—	0.008	300	20
RF p-type layer:	—	—	0.1	—	80	—	8	3	1.8	—	0.07	300	10
RF n-type layer:	2.0	—	—	—	70	8	—	—	1.2	—	0.07	320	10

TABLE 21-continued

(Comparative Example 2)

	SiH_4 Flow rate (sccm)	Si_2H_6 Flow rate (sccm)	CH_4 Flow rate (sccm)	GeH_4 Flow rate (sccm)	H_2 Flow rate (sccm)	PH_3/H_2 Flow rate (sccm)	B_2H_6/H_2 Flow rate (sccm)	SiH_4/H_2 Flow rate (sccm)	Pressure (Torr)	MW power (W/cm^3)	RF power (W/cm^3)	Substrate temp. (° C.)	Layer thickness (nm)
MW i-type layer:	50	—	—	35	250	—	—	—	0.02	0.1	0.205	320	140
RF p-type layer:	—	—	0.2	—	80	—	8	3	1.8	—	0.07	250	10
RF n-type layer:	1.3	—	—	—	50	10	—	—	1.05	—	0.04	230	10
RF i-type layer:	—	2.0	—	—	100	—	—	—	0.8	—	0.007	180	90
RF p-type layer:	—	—	0.4	—	90	—	8	3	1.6	—	0.07	170	10

[0279]

TABLE 2

Sample	Stabilized conversion efficiency	Rate of deterioration by light	Rate of heat-resistance deterioration	Cell breakdown voltage	Yield
SCEx-2	1	1	1	1	1
SCCp-2	0.92	1.12	1.13	0.97	0.99

[0280]

TABLE 3

	Layer thickness of i-type layer of 2nd p-i-n: (μm)							
	0.3	0.5	0.7	1	1.2	1.5	1.8	2.0
Initial photoelectric conversion efficiency:	C	A	A	A	A	A	B	B
Fill factor:	B	B	A	A	A	A	B	C
Rate of deterioration by light	B	A	A	A	A	A	B	B

A: Optimum for practical use
B: Sufficient for practical use
C: Insufficient for practical use

[0281]

TABLE 4

	Layer of thickness of i-type layer of 3rd p-i-n: (μm)							
	1	1.5	2	2.5	3	3.5	3.8	4.0
Initial photoelectric conversion efficiency:	C	A	A	A	A	A	B	C
Fill factor:	B	A	A	A	A	A	B	C
Rate of deterioration: by light	B	A	A	A	A	A	B	B

A: Optimum for practical use
B: Sufficient for practical use
C: Insufficient for practical use

[0282]

TABLE 5

	Boron (B) content in i-type layer of 2nd p-i-n: (ppm)				
	0	1	3	8	10
Initial photoelectric conversion efficiency:	A	A	A	B	C
Stabilized photoelectric conversion efficiency:	A	A	A	B	B
Rate of deterioration by light:	A	A	A	A	B
Rate of heat-resistance deterioration:	A	A	A	A	B

A Optimum for practical use
B Sufficient for practical use
C Insufficient for practical use

[0283]

TABLE 6

	Boron (B) content in i-type layer of 3rd p-i-n: (ppm)				
	0	1	3	8	10
Initial photoelectric conversion efficiency:	A	A	A	B	C
Stabilized photoelectric conversion efficiency:	A	A	A	B	B
Rate of deterioration by light:	A	A	A	A	B
Rate of heat-resistance deterioration:	A	A	A	A	B

A Optimum for practical use
B Sufficient for practical use
C Insufficient for practical use

[0284]

TABLE 71

(Comparative Example 7)

	SiH_4 Flow rate (sccm)	Si_2H_6 Flow rate (sccm)	CH_4 Flow rate (sccm)	GeH_4 Flow rate (sccm)	H_2 Flow rate (sccm)	PH_3/H_2 Flow rate (sccm)	B_2H_6/H_2 Flow rate (sccm)	SiH_4/H_2 Flow rate (sccm)	Pressure (Torr)	MW power (W/cm^3)	RF power (W/cm^3)	Substrate temp. (° C.)	Layer thickness (nm)
RF n-type layer:	2.2	—	—	—	80	10	—	—	1.3	—	0.05	380	10
RF i-type layer:	—	3.5	—	—	100	—	—	—	0.65	—	0.008	300	10
MW i-type layer:	48	—	—	51	170	—	—	—	0.01	0.1	0.32	380	170
RF i-type layer:	—	3.5	—	—	100	—	—	—	0.65	—	0.008	300	23
RF p-type layer:	—	—	0.1	—	80	—	9	3	1.8	—	0.07	300	10
RF n-type layer:	1.8	—	—	—	70	8	—	—	1.2	—	0.008	320	10
MW i-type layer:	80	—	—	—	350	—	—	—	0.02	0.1	0.205	300	350
RF p-type layer:	—	—	0.2	—	80	—	9	3	1.7	—	0.07	260	10
RF n-type layer:	1.1	—	—	—	50	10	—	—	1.05	—	0.04	230	10
RF i-type layer:	—	2.0	—	—	200	—	—	—	0.8	—	0.007	190	90
RF p-type layer:	—	—	0.4	—	90	—	8	3	1.6	—	0.07	170	10

[0285]

TABLE 7

Sample	Stabilized conversion efficiency	Rate of deterioration by light	Rate of heat-resistance deterioration	Cell breakdown voltage	Yield
SCEx-7	1	1	1	1	1
SCCp-7	0.88	1.20	1.15	0.99	0.99

[0286]

TABLE 8

Optical absorption cefficient at 950 nm of i-type layer of 2nd p-i-n: (cm-1)	≦10	100	200	400
Initial photoelectric conversion efficiency:	C	C	A	A
Stabilized photoelectric conversion efficiency:	C	B	A	A
Rate of deterioration by light:	C	C	A	A
Rate of heat-resistance deterioration:	C	B	A	A

A: Optimum for practical use
B: Sufficient for practical use
C: Insufficient for practical use

[0287]

TABLE 9

Optical absorption coefficient at 950 nm of i-type layer of 3rd p-i-n: (cm-1)	≦10	100	200	400
Initial photoelectric conversion efficiency:	C	C	A	A
Stabilized photoelectric conversion efficiency:	C	C	A	A
Rate of deterioration by light:	C	B	A	A
Rate of heat-resistance deterioration:	C	B	A	A

A: Optimum for practical use
B: Sufficient for practical use
C: Insufficient for practical use

[0288]

TABLE 101

(Example 10)

	SiH_4 Flow rate (sccm)	Si_2H_6 Flow rate (sccm)	CH_4 Flow rate (sccm)	GeH_4 Flow rate (sccm)	H_2 Flow rate (sccm)	PH_3/H_2 Flow rate (sccm)	B_2H_6/H_2 Flow rate (sccm)	SiH_4/H_2 Flow rate (sccm)	Pressure (Torr)	MW power (W/cm^3)	RF power (W/cm^3)	Substrate temp. (° C.)	Layer thickness (nm)
RF n-type layer:	2.2	—	—	—	75	10	—	—	1.3	—	0.05	380	10
RF n-type layer:	0.2	—	—	—	100	5	—	—	0.65	—	0.1	290	13
MW i-type layer:	48	—	—	—	1,600	—	—	—	0.05	0.10	0.32	300	3,000
RF i-type layer:	—	4.0	—	—	100	—	—	—	0.65	—	0.008	290	23
RF p-type layer:	—	—	0.1	—	80	—	9	4	1.8	—	0.08	300	10
RF n-type layer:	0.2	—	—	—	150	8	—	—	0.7	—	0.08	320	100
MW i-type layer:	80	—	—	—	1,300	—	—	—	0.1	0.15	0.12	300	1,000
RF p-type layer:	—	—	0.2	—	80	—	9	4	1.7	—	0.08	260	10
RF n-type layer:	1.1	—	—	—	50	10	—	—	1.05	—	0.04	220	10
RF i-type layer:	—	2.0	—	—	200	—	—	—	0.8	—	0.007	190	90
RF p-type layer:	—	—	0.4	—	90	—	8	3	1.6	—	0.08	160	10

[0289]

TABLE 10

Sample	Stabilized conversion efficiency	Rate of deterioration by light	Rate of heat-resistance deterioration	Cell breakdown voltage	Yield
SCEx-10	1	1	1	1	1
SCCp-10	0.89	1.21	1.14	0.99	0.98

What is claimed is:

1. A stacked photovoltaic device comprising at least three p-i-n junction constituent devices superposed in layers, each having a p-type layer, an i-type layer and an n-type layer which are formed of silicon type non-single crystal semiconductors, wherein;

an amorphous silicon layer is used as the i-type layer of a first p-i-n junction, a microcrystalline silicon layer is used as the i-type layer of a second p-i-n junction and a microcrystalline silicon layer is used as the i-type layer of a third p-i-n junction; the first to third p-i-n junction layers being in the order from the light-incident side.

2. The stacked photovoltaic device according to claim 1, wherein the microcrystalline silicon layer which is the i-type layer of the second p-i-n junction has a layer thickness in the range of from 0.5 μm to 1.5 μm.

3. The stacked photovoltaic device according to claim 1, wherein the microcrystalline silicon layer which is the i-type layer of the third p-i-n junction has a layer thickness in the range of from 1.5 μm to 3.5 μm.

4. The stacked photovoltaic device according to claim 1, wherein the microcrystalline silicon layer which is the i-type layer of the second p-i-n junction contains boron, and the boron is in a content not more than 8 ppm.

5. The stacked photovoltaic device according to claim 1, wherein the microcrystalline silicon layer which is the i-type layer of the third p-i-n junction contains boron, and the boron is in a content not more than 8 ppm.

6. The stacked photovoltaic device according to claim 1, wherein the n-type layer of the second p-i-n junction comprises microcrystalline silicon.

7. The stacked photovoltaic device according to claim 1, wherein the n-type layer of the second p-i-n junction comprises a double layer consisting of a microcrystalline silicon layer and an amorphous silicon layer.

8. The stacked photovoltaic device according to claim 1, wherein the n-type layer of the third p-i-n junction comprises microcrystalline silicon.

9. The stacked photovoltaic device according to claim 1, wherein the n-type layer of the third p-i-n junction comprises a double layer consisting of a microcrystalline silicon layer and an amorphous silicon layer.

10. The stacked photovoltaic device according to claim 1, wherein the microcrystalline silicon layers which are the i-type layers of the second and third p-i-n junctions each have an optical absorption coefficient of 200 cm^{-1} or above at 950 nm.

11. The stacked photovoltaic device according to claim 1, wherein the microcrystalline silicon layer which is the i-type layer of the second p-i-n junction is formed by plasma chemical vapor deposition using a high frequency power of from 0.1 GHz to 10 GHz.

12. The stacked photovoltaic device according to claim 1, wherein the microcrystalline silicon layer which is the i-type layer of the third p-i-n junction is formed by plasma chemical vapor deposition using a high frequency power of from 0.1 GHz to 10 GHz.

13. The stacked photovoltaic device according to claim 1, which is formed by a roll-to-roll system in which the layers are superposed while transporting a continuous substrate stretched over a pair of rolls.

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